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Enhanced Intensities of the Ligand-to-Metal Charge-Transfer Transitions in Ru(III) and Os(III) Complexes of Substituted Bipyridines

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Ru(III) and Os(III) complexes of 2,2'-bipyridine carrying electron-donor substituents show fairly intense ligand-to-metal charge-transfer (LMCT) absorption band(s) in the red/near-IR region. The intensity of the LMCT band increases with increasing effective donor strength of the substituted bpy ligand. The variations in the energies and intensities of these LMCT bands has been examined in twenty complexes of the type $M(X_2-bpy)_3$ and $M(bpy)_n(X_2-bpy)_{3-n}$ (M = Ru or Os, X = Me, OMe, NH₂, and NMe₂). In the homo trischelates the energy of the low-energy LMCT transition falls within a narrow range of 1.80 \pm 0.1 V for Ru(III) and 2.20 \pm 0.1 V for Os(III). The energy of the LMCT transition is much lower in mixed-ligand complexes. A quantitative analysis as a function of donor strength and Hammett substituent constants is presented.

Introduction

Charge-transfer (CT) excited states play an important role in the observed photoreactivity of metal complexes. Early studies of CT photochemistry have been on cobalt(III) complexes. ^{1,2} The last 2 decades witnessed an enormous progress in our understanding of the spectroscopy and photophysics of polypyridine complexes of transition metals. ^{3,4} For the polypyridine complexes of Ru(II) and Os(II) (octahedral, low-spin, d⁶ electronic configuration), the lowest excited state invariably is of the metal-to-ligand charge transfer (MLCT) type: $[(d_{\pi}^{-6}) \rightarrow (d_{\pi}^{-5})(\pi_L^{+1})]$ and the intense color of these complexes is due to these CT transitions. The emissive nature and redox reactivity of these MLCT excited states in fluid solutions allowed extensive quantitative studies be made on the factors that determine the properties of such CT transitions.

The Ru(III) and Os(III) complexes (also octahedral, low spin, with d⁵ electronic configuration) in general show ligand-to-metal $(\pi_L \to t_{2g}^5)$ charge-transfer (LMCT) transitions in the visible light region. Much less is known on these LMCT states of these complexes, 5-12 possibly due to their very weak intensities ($\epsilon \le 500 \, \mathrm{M}^{-1} \, \mathrm{cm}^{-1}$) in the widely studied complexes Ru(bpy)₃³⁺, Os-(bpy)₃³⁺, and their nonemissive nature. Two key investigations of electronic spectra are those of Bryant and Ferguson⁶ and of Koher. 8

As part of our studies on dye sensitization of semiconductor electrodes^{13,14} and applications of polypyridine complexes as redox mediators in biosensors, ¹⁵ recently we examined a number of polypyridine complexes of Ru and Os. Of particular importance to this work are the complexes with electron donor substituents such as 4,4'-(dimethylamino)- or 4,4'-dimethoxybipyridine. The electron-donating capacity of the bipyridine (bpy) is greatly enhanced in these complexes that the M(II) \rightarrow M(III) oxidation occurs readily in solution ($E_{3+/2+} \leq 0.5$ V). Generally, low-energy LMCT transitions are favorable when the metal is oxidizing and the ligand reducing. For this reason, the above complexes appeared to be ideal candidates to probe LMCT transitions.

It has been found that Ru(III) and Os(III) complexes with donor substituents at the 4,4' position of 2,2'-bipyridine ligand showed fairly intense ligand-to-metal CT bands in the red-to-near-IR region (an order of magnitude more intense than that observed in the parent/unsubstituted bpy complex!). We have examined the properties of such CT bands by a systematic tuning of the donor strength of the bipyridine ligand using different substituents (see structures shown below). A series of about 20

complexes of both metal ions has been studied. Herein we present our results for a number of homo tris- and mixed ligand complexes and some rationalization of the observed trends in the energy and intensity of LMCT transitions.

4,4'-disubstituted 2,2'-bipyridine

R = H (bpy)
R = Me (DM-bpy)
R = OMe (DMO-bpy)
R = NH₂ (DA-bpy)
R = NMe (DMA-bpy)

Experimental Section

Materials. Disubstituted bipyridine ligands such as 4,4'-dimethoxy (DMO-bpy), 4,4'-diamino (DA-bpy), 4,4'-(dimethylamino) (DMA-bpy), and 4,4'-dimethyl (DM-bpy) and their Ru(II) complexes were prepared as described in the literature. 16,17 [Ru(bpy)₃]Cl₂and [Ru(bpy)(4,7-dihydroxy-1,10-phenanthroline)₂]-Cl₂ complexes were available from our earlier work. 18 Chemical oxidants used (Br₂ and ceric ammonium nitrate) were analytical grade chemicals from Fluka and were used as supplied.

Methods. Absorption spectra of the Ru(II) and Ru(III) complexes were recorded in 1-cm quartz cells on a Cary 5 spectrophotometer. The Ru(II) complexes were oxidized by adding controlled quantities of concentrated oxidants (Br₂ or Ce(IV)) in water or in acetonitrile. One-electron oxidation potentials of the complexes were determined by cyclic voltammetry in a conventional three-electrode cell. Electrochemical studies were carried out in acetonitrile containing 0.1 M LiClO₄ with a glassy carbon or Pt working electrode and a SCE reference electrode. Quoted are formal/midpoint potentials measured in acetonitrile vs SCE. It has been shown earlier that, ¹⁹ within \pm 50 mV, $E_{1/2}$ values of polypyridine complexes of Ru and Os measured in CH₃CN vs SCE and $E_{1/2}$ values measured in water vs NHE are the same. Estimated error is \pm 10% in the reported molar absorbances and \pm 50 mV for the redox potentials.

Results

The charge-transfer bands in the UV-visible absorption spectra were determined for a number of ruthenium and osmium with the metal ion formally in the 2+ and 3+ state. Both homo- and mixed-ligand chelates containing one or more electron-donor type

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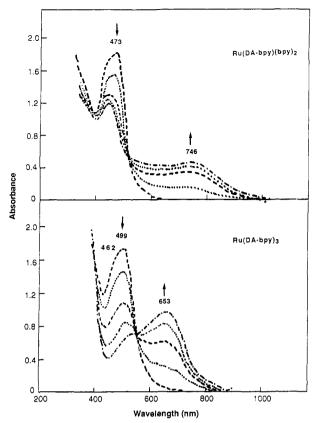


Figure 1. Absorption spectral changes observed during the oxidation of Ru(II) complexes Ru(DA-bpy)₃²⁺ (bottom) and Ru(DA-bpy)(bpy)₂²⁺ (top) using Ce(IV) as an oxidant in acetonitrile solutions.

polypyridine ligands were studied. The charge-transfer nature of the visible absorption bands can be readily noted from the solvent dependence of these maxima. In Os(DA-bpy)₃³⁺, for example, the LMCT band in the 400-nm region gradually red shifts along the series H₂O (389 nm), CH₃CN (394 nm), CH₃-COCH₃ (396 nm), DMF (407 nm), and DMSO (409 nm). The series represent solvents of increasing donor number (DA). The solvatochromic behaviour of the LMCT band observed in [RuIII-(NH₃)₅(4-Me₂N-py)]³⁺ has been studied earlier by Curtis Meyer.¹² The CT transition energy increases linearly with the electron-pair-donor ability of the solvent, as represented by the donor number. Figures 1 and 2 present a comparison of the absorption spectra of two Ru and Os complexes in the two oxidation states: [Ru(DA-bpy)₃], [Ru(bpy)₂(DA-bpy)], [Os-(DMA-bpy)₃], and [Os(DMA-bpy)₂(bpy)]. The absorption spectra show clearly that the LMCT band has gained considerable intensity in these complexes with donor ligands as compared that observed in the parent bpy complex, M(bpy)₃³⁺.

The complexes in the 3+ were obtained in solution by chemical oxidation using oxidants such as bromine or Ce(IV). The oxidation is clean and quantitative as seen by the observance of isosbestic points during the oxidation (cf. Figure 1). In all cases, the CT absorption of divalent complexes in the visible light region is replaced by one or more ligand-to-metal charge-transfer bands. The LMCT bands are red-shifted and in some cases have their maxima as low as 970 nm. Bpy complexes of Ru(II) and Os(II) complexes with strong donor ligands such as -NH2 or -NMe2 are readily oxidized by molecular oxygen. In fact air oxidation occurs readily in all complexes with $E_{3+/2+} \le 0.35$ V. The relative concentrations of M(II) and M(III) species were assessed in each case by adding dithionite to degassed solutions and measuring the absorption spectra. This was necessary especially for osmium complexes due to extensive overlap of the MLCT bands of Os(II) with LMCT bands of Os(III) in the visible light region. Also addition of excess oxidant (Br2) was avoided as this led to further

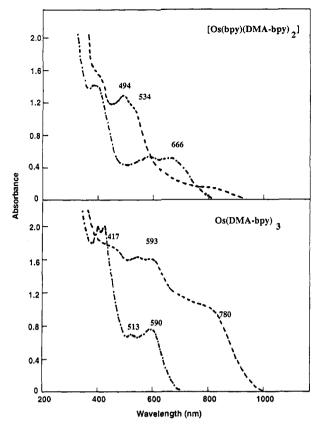


Figure 2. Comparison of the absorption spectra of Os(II) (---) and Os(III) (---) complexes Os(DMA-bpy)₃(bottom) and Os(DMA-bpy)₂-(bpy) (top) using Br₂ as an oxidant in acetonitrile solutions.

oxidation of Os(III) complexes to yet unidentified species (possibly Os(IV)?). Table I summarizes the absorption spectral data obtained in this work.

Oxidation potentials of the complexes were determined in acetonitrile or DMF by cyclic voltammetry and these are listed in Table II. Except for those with strong electron-donor ligands, a single reversible oxidation wave can be observed in the anodic scan (up to 1.5V). [In supercritical solvents it is possible to extend considerably the anodic scan range, and Bard et al.20 have used this technique to observe successive oxidation of the trischelates $M(bpy)_3$, M = Fe, Ru, and Os.] This is assigned to $M(II) \rightarrow$ M(III) oxidation as the electrolysis product is identical to that obtained using mild chemical oxidants. The complexes are listed in the order of increasing redox potentials, $E_{3+/2+}$. Replacement of a bpy ligand in the M(bpy)₃²⁺ by one or more of the electronrich ligands increases the effective charge density at the metal and facilitates its oxidation. The more the number of donor ligands present much larger is the shift in the E_{ox} values. For example, replacement of a bpy by a DMA-bpy ligand facilitates oxidation by ca. 350 mV and with three DMA-bpy, the first oxidation occurs more readily by ca 1.10 V.

MLCT transitions of the Ru(II) and Os(II) complexes are fairly well understood, and hence we will mention only a few important points. In both cases, with increasing donor strength of the substituent X, the MLCT transition moves to lower energies. In the ruthenium complexes, for a tuning of the oxidation potential over 1 V, the shift in the MLCT energy is only about a third (0.34 V). In the osmium complexes, For a comparable tuning in $E_{3+/2+}$ potential, the MLCT transition of Os complexes show more pronounced shift (\approx 0.5 V). The differences between the two metal complexes can be rationalized in terms of relative importance of back-bonding in each case.

When discussing trends in the energy and intensity of CT transitions, it is important to keep track of the ligand involved in the CT process. In mixed ligand complexes of the type

TABLE I: Energies and Intensities of Lowest Energy MLCT (of M(II)) and LMCT (of M(III)) Transitions in Polypyridine Complexes of Ru and Os in Aqueous Solution at Room Temperature

complex	$\sigma_{ m p}^+$	M(II)-LL CT**		LL-M(III) CT	
		λ _{max} (nm)	ε (M ⁻¹ cm ⁻¹)	λ _{max} (nm)	ε (M ⁻¹ cm ⁻¹)
Ru(DMA-bpy) ₃	-1.7	518 (10560)	480 (8420)	683 (5820)	580 (4365)
Ru(DOH-phen) ₂ (bpy)		470 (13070)	400 (9300)	972 (4010)	670 (3270)
Ru(DA-bpy) ₃	-1.3	499 (8040)	462 (7160)	653 (4390)	526 (3160)
Ru(DOH-phen) ₂ (DA-bpy)	-1.05	460 (11400)	440 (10800)	809 (2280)	676 (1710)
Ru(DA-bpy) ₂ (bpy)	-0.87	488 (10300)	446 (10350)	725 (4020)	594 (4130)
Ru(DMO-bpy) ₃	-0.78	488 (10890)	460 ((9530)	730 (5150)	565 (3150)
Ru(DOH-phen)(bpy) ₂	0.61	495 (12000)	471 (13100)	973 (4060)	658 (3435)
Ru(DA-bpy)(bpy) ₂	-0.43	473 (12080)	445 (11100)	746 (3410)	596 (2860)
Ru(DMO-bpy)(bpy) ₂	-0.26	464 (9010)	436 (8335)	841 (2160)	690 (560)
Ru(DM-bpy) ₃	-0.31	460 (17000)	430 (14500)	642 (480)	555 (250)
Ru(bpy) ₃	0	453 (14500)	• • •	675 (750)	
Os(DMA-bpy) ₃	-1.7	593 (14400)	548 (13370)	590 (6290)	513 (5705)
Os(DA-bpy) ₃	-1.3	553 (15880)	516 (15880)	527 (5350)	465 (5795)
Os(DMA-bpy) ₂ (DM-bpy)	-1.23	538 (11490)	499 (12720)	648 (5210)	562 (6510)
os(DMA-bpy) ₂ (bpy)	-1.10	534 (10970)	494 (12430)	666 (4850)	565 (4565)
Os(DA-bpy) ₂ (DMbpy)	-0.97	529 (9180)	488 (10075)	586 (3210)	508 ((3700)
Os(DEO-bpy) ₃	-0.80	513 (9700)	475 (10050)	450 (4750)	(()
Os(DMO-bpy) ₃	-0.78	516 (6800)	475 (7140)	430 (4100)	
Os(DM-bpy) ₂ (DA-bpy)	-0.64	507 (18765)	460 (18765)	596 (3830)	508 (3480)
Os(DM-bpy) ₃	-0.31	, ,	` ,	536 (603)	(2.117)
Os(bpy) ₃	0	478 (11100)	436 (10700)	563 (585)	
$Ru(2,2'-BiImH_2)_3^a$		401 (12000)	≈380 `	760 (2500)	
$Ru(2,2'-BiImH_2)_2(bpy)^a$		487 (5000)	≈450	853 (2100)	
$Ru(2,2'-BiImH_2)(bpy)_2^a$		473 (9300)	432 (7100)	1000 (800)	
Ru(2,2'-BiBzImH2)3b		483 (10000)	≈ 450	745 (2000)	
$Ru(2,2'-BiBzImH_2)_2(bpy)^b$		465 (11000)	≈440	820 (1900)	
$Ru(2,2'-BiBzImH_2)(bpy)_2^b$		463 (12000)	438 (13000)	780?? (990)	

^a Data taken from ref 19a. ^b Data taken from ref 19b.

TABLE II: Redox Potentials (in volts, vs SCE) for One-Electron Oxidation of Polypyridine Complexes of Ru(II) and Os(II) in Acetonitrile

complex	$E_{ox}(1)$	complex	$E_{ox}(1)$	$E_{\rm ox}(2)$
Ru(DMA-bpy) ₃	+0.15	Os(DMA-bpy) ₃	-0.16	+1.00
Ru(DO-phen) ₂ (bpy)	+0.15	Os(DA-bpy) ₃	-0.11	+1.15
Ru(DA-bpy) ₃	+0.35	Os(DMA-bpy) ₂ (DM-bpy)	+0.10	+1.30
Ru(DOH-phen) ₂ (DA-bpy)	+0.50	Os(DMA-bpy)2(bpy)	+0.15	+1.25
Ru(DA-bpy) ₂ (bpy)	+0.60	$Os(DA-bpy)_2(DM-bpy)$	+0.25	
Ru(DMO-bpy) ₃	+0.80	Os(DEO-bpy) ₃	+0.32	
Ru(DOH-phen)(bpy) ₂	+0.90	Os(DMO-bpy) ₃	+0.385	
Ru(DA-bpy)(bpy) ₂	+0.95	Os(DM-bpy) ₂ (DAbpy)	+0.40	
Ru(DMO-bpy)(bpy) ₂	+1.05	$Os(DM-bpy)_3$	+0.60	
Ru(DM-bpy) ₃	+1.10	Os(bpy) ₃	+0.80	
Ru(bpv)	+1.26	· • • • • • • • • • • • • • • • • • • •		

 $[M(bpy)_n(LL)_{3-n}]$, the MLCT transition involves the acceptor ligand (bpy). The LMCT transition on the contrary involves the electron-rich donor ligand LL (substituted bpy, biimidazole (BiIm), or bibenzimidazole (BiBzIm)). Fairly intense absorption in the red/near-IR region has been noted recently in the spectra of mixed ligand complexes of Ru(III) containing electron-rich donor ligands such as bibenzimidazole²¹ and triazoles²² and they have been assigned to ligand-to-metal charge transfer. For comparison, we have included the LMCT absorption spectral data of BiIm complexes in Table I.

Examination of the data presented in Table I and II reveals useful trends in the energy and intensities of the LMCT transitions: (i) The lowest energy LMCT transition of the trischelates is observed within a narrow range of 1.80 ± 0.1 eV for Ru(III) and 2.20 \pm 0.1 eV for Os(III) in spite of the wide variation of $E_{3+/2+}$ values. (ii) In mixed ligand chelates, the LMCT transition occurs at lower energies than in the homotrischelates. This can be seen clearly in the absorption spectra shown in Figures 1 and 2. (iii) The intensity of the LMCT transition increases with decreasing values of the redox potential, E[Ru(III)/Ru(II)]. The first point is reminiscent of the near isoenergetic MLCT transition observed in Ru(bpy)₃²⁺ and Ru-(bpz)₃²⁺ complexes. In the latter complex, 0.5V anodic shift of the E_{ox} is accompanied by similar shifts in the first reduction potential.

The absorption spectra of the trivalent complexes in the 400-1000-nm region consisting of several broad bands that are overlapping. Using a gaussian fit analysis, various band maxima and their relative intensities determined. Table III presents a summary of the derived data on different bands that have been identified.

Discussion

Assignments of the Absorption Spectra of M(III) Complexes. The absorption spectra of the trivalent complexes can be broadly divided into three regions and their features can be outlined as follows: The first region, above 500 nm, consist of low-energy LMCT transition(s) ($\pi_L \rightarrow d\pi(t_{2g})$ bands with molar absorbance, $\epsilon \le 7000 \text{ M}^{-1} \text{ cm}^{-1}$. Spectral analysis reveals two bands of approximately equal intensity in the low-energy (≥500 nm) region for the Ru and Os complexes. In all cases, there is a gradual increase in intensity of these bands with increasing donor strength of the substituents.

Then further up, in the 350-500-nm region, in principle, one or more of the following transitions can have energies falling in this range: LMCT of the type: $\pi_{LL} \rightarrow d_{\pi}$ (e_g) and MLCT of the type: $d_{\pi}(t_{2g}) \rightarrow \pi^*_{LL}$. By analogy to that observed in M(II) complexes, the MLCT bands involving M(III)'bpy/LL transitions are expected to be more intense ($\epsilon \le 15\,000\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$). Spectral

TABLE III: LMCT Transitions of Polypyridyl Complexes of Ru(III) and Os(III)^a

		MLCT $(d_{\pi} \rightarrow \pi^*_L)$		
complex	I	II	III	IV IV
Ru(DMAbpy)3]	13900 (5820) 1730	16400 (4365) 1760	18900 (4365) 1700	25000 (17620)
Ru(DAbpy) ₃]	15350 (4390) 2000	19000 (3160) 2050	22200 (2570) 1900	27500 (11710)
[Ru(DOHphen) ₂ (DAbpy)]	12400 (2280) 1420	14800 (1710) 1230	16700 (1480) 1210	19500 (7070), 24400 2116
[Ru(DOHphen) ₂ (bpy)]	10300 (4010) 1860	15200 (3390) 2855	18400 (1540) 2100	22100 (7200), 25700 2700
[Ru(DMObpy) ₃]	13800 (5150) 2450	17700 (3150) 2050		26200 (12875)
[Ru(bpy) ₂ (DAbpy)]	13400 (3410) 2020	16800 (2860)) 1900		23000
[Ru(bpy) ₂ 9DMObpy)]	11950 ((2160)) 1700	14500 (560) 1650		21740, 23470
[Ru(DMbpy) ₃]	15500 (480) 1690	18020 (250)		22800 (4800) 1700
[Os(DMAbpy) ₃]	16800 (6290) 1330	19500 (5705) 1600		24000 (17900) 26000 (17900)
[Os(DAbpy) ₃]	19200 (5350) 1450	21500 (5795) 1460		25640 (19840)
[Os(DMAbpy) ₂ (DMbpy)]	15500 (5210) 1500	17800 (6510) 1530	20200 (4490) 1470	25000 (17230) 26000 (17230)
[Os(DMAbpy) ₂ (bpy)]	15000 (4850) 1600	17700 (4565) 1600	20000	25970 (13030)
$[Os(DAbpy)_2(DMbpy)]$	17100 (3210) 1488	19700 (3700) 1620		26810 (10870)
$[Os(DAbpy)(DMbpy)_2]$	17100 (3830) 1600	19700 (3480) 1600		25900 (16360) 28500 (12890)

^a Shown are ν_{max} (in cm⁻¹) values with molar absorptivities in parentheses followed by bandwidth ($\Delta \nu$, in cm⁻¹).

analysis allows identification of two bands in this intermediate energy region, with molar absorbances at least thrice as intense as the LMCT bands observed above 500 nm. With strong donor ligands, $M(III) \rightarrow M(IV)$ can occur at potentials below 2 V. This can give rise to MLCT transitions with energies in the range 2.5-3.5 eV, especially in mixed ligand complexes containing one or more of the parent bpy ligand. In fact, oxidation occurs in the potential range +1.0 to +1.3 V for the complexes $[Os(DMA)_n-(bpy)_{3-n}]$ and $[Os(DA-bpy)_n(bpy)_{3-n}]$, n=1, 2, and 3. In the mixed ligand complexes with strong electron-donor and -acceptor ligands, there can be interligand charge transitions (LLCT) as well.

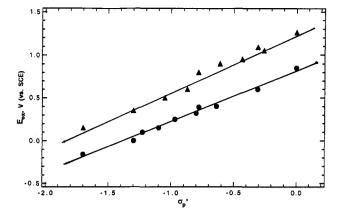
Finally, in the UV region (≤ 350 nm), there are mainly intraligand ($\pi-\pi^*$) transition bands ($\epsilon \geq 25\,000\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$). This region is similar to that observed in M(II) complexes. In his doctoral dissertation,⁸ Kober examined the electronic absorption spectra of a number of mixed ligand complexes of Os(III), [Os-(bpy)₂X₂], X = Cl, Br, py, MeCN, Ph₃P, CO, and Ph₂MeP. Weak bands ($\epsilon \approx 500-1000\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) in the 17 000-21 000-cm⁻¹ region were assigned to bpy(π)-Os(d π) CT transitions. These are followed (in increasing energy) by halide-Os(d π) CT transitions ($\epsilon \approx 2000-6000\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) in the 27 000-28 500-cm⁻¹ range and Os(d π)-bpy(π^*) MLCT transitions ($\epsilon \approx 3800-6000\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) in the 2488-28 000-cm⁻¹ range.

Rationalization of LMCT State Energies in Homotrischelates, $M(LL)_3^{3+}$. The LMCT transitions involve electronic transitions between donor orbitals that are largely $\pi(X$ -bpy) in character to acceptor orbitals that are largely $d\pi$ in character. With increasing electron donating character of the substituent X, the electron-donating ability of the $\pi(X$ -bpy) orbitals is enhanced and this effect is transmitted to the metal $d\pi$ -orbitals by via $d\pi$ - $\pi(LL)$ mixing. The oxidation potential data shows that there is a corresponding ease of oxidation of the metal center from +2 to +3 state. This arises from a decrease in the π - d_{π} back-bonding which makes the metal more electron rich. Interestingly the effect on the $d\pi$ -orbitals is nearly the same as in the π -orbitals even though the substituent changes are made in the ligand. The shift in E_{0x} values for the M(II/III) couples $(X = NMe_2 \text{ to } H)$ is $\approx 1.0 \text{ V}$.

The above qualitative discussion of substituent effects on energy levels can be put on a quantitative basis using Hammett substituent values for various substituents employed.²³ The LMCT transition involves promotion of an electron from the HOMO of the donor ligand to one of the partially filled t_{2g} orbitals of the metal ion: $\pi_L \rightarrow t_{2g}^{5}(M)$. The longest wavelength absorption maxima of the CT band in the red/near-IR region has been used to deduce the energy of the lowest energy LMCT transition. To a first approximation, the energy of the acceptor t_{2g} orbital can be estimated using the first oxidation potential, E[Ru(III)/Ru(II)]. The Hammett substituent constant σ_p^+ can be used as a measure of the relative donor strength of the substituted bpy ligand. (Correlations use σ_p^+ instead of σ_p , for the latter values are more applicable for the cases where the substituent group interacts with the developing positive charge). Figure 3 (top) shows the dependence of the measured E_{ox} values of various 4,4'-(X)₂-2,2'bpy complexes of Ru, Os with the σ_p + values of the corresponding substituent X. A linear correlation can be observed between the first oxidation potential and the Hammett substituent constant σ_p^+ . The data points include the entire collection (20) of Ru and Os complexes. For mixed-ligand complexes of the type $[M(LL)_n(LL')_{3-n}]$ 3+, an overall effective substitution constant σ^+_{eff} was used (a weighted sum of the individual substituents/ligands: $\sigma^{+}_{eff} = [n\sigma^{+}_{LL} + (3 - n)\sigma^{+}_{LL'}]/3)$.

The energy of the donor level (π_L) in the Ru and Os complexes is not directly accessible. We have attempted to estimate it using the energy of the LMCT transition and experimentally measured $E_{\rm ox}$ values of the respective trischelates, M(LL)₃³⁺. To a first approximation, the first oxidation potential, $E_{\rm ox}$ can be taken as a measure of the acceptor ($t_{\rm 2g}$ level of the metal). The spectroscopic (0–0) energy of the CT transition has been estimated as the energy at which the absorption intensity of the lowest energy band drops to 1% of the intensity at the band maximum on the high energy side of the band. This point is given by $\nu_{1\%} = \nu_{\rm max} + 1.29 \Delta \nu_{1/2}$, where $\Delta \nu_{1/2}$ is the bandwidth at half-height for a Gaussian band shape.²⁴

For a given donor ligand, the estimated π_L value for the Ru and Os complexes differ only by ± 50 mV. Figure 3 (bottom) shows that the dependence of the ligand π_L level with the



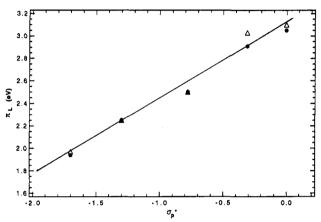


Figure 3. Top: dependence of first oxidation potential with the Hammett substitution constant σ^+ for a series of substituted bpy complexes of Ru-(III) (filled triangles) and of Os(III) (filled circles). Bottom: variation of the estimated energy level of the substituted bpy ligand HOMO π_{LL} with the Hammett substituent constant σ^+ in a series of complexes of Ru(III) (open triangles) and Os(III) (filled circles).

substituent constant σ^+ . As expected, the ligand π_L level shifts linearly with increasing donor strength of the substituted bpy ligand. The data points include the trischelates only, since in these systems there is no ambiguity on the identity of the donor ligands involved in the LMCT transition. In the trischelates of Ru and Os, the donor (π_L) orbital and the acceptor (t_{2g}) vary linearly but in a parallel fashion. This accounts for the nearisoenergetic values of the LMCT transition energies in the trischelates of both Ru and Os.

Rationalization of LMCT State Energies in Mixed Chelates, [M(LL)_a(LL')_{3-a}³⁺. In mixed ligand complexes, the LMCT transition occurs at lower energies than that observed in the trischelates. In a series of mixed ligand complexes, [Ru- $(LL)_{3-n}(LL')_n$ ³⁺ (n = 1-3), replacement of a donor ligand LL by a poorer donor/acceptor ligand LL causes a red-shift of the observed LMCT transition. The shift is proportional to the extent of the replacement. Since the first oxidation potential accurately describes the overall electron donation, we examined the variation of the LMCT maximum with the oxidation potential of the mixed ligand complex. Figure 4 shows such a plot for some select Ru complexes. A linear plot is obtained for each donor ligand. Figure 4 also includes data for the mixed ligand Ru complexes derived from 2,2'-biimidazole (BiImH₂) and 2,2'-bibenzimidadzole (Bi-BzImH₂), where moderately intense LMCT bands have been reported earlier.

The lowering of the LMCT energy in mixed ligand complexes is caused by back-bonding effects. 25 Figure 5 attempts to provide a basis for this observation in terms of the extent of shifting of the donor and acceptor orbitals in the mixed ligand complexes. Shown in the figure are the estimated π_L and t_{2g} levels for the two trischelates Ru(bpy)₃³⁺, Ru(DA-bpy)₃³⁺ and a mixed ligand

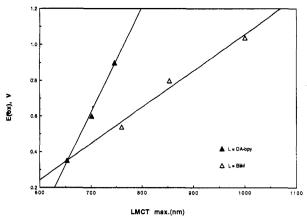


Figure 4. Variation of the LMCT absorption maximum with the first oxidation potential for a series of substituted bpy complexes of Ru(III).

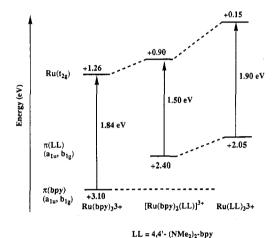


Figure 5. Schematic correlation of the LMCT transition energies with the energies of the related metal and ligand orbitals.

complex [Ru(bpy)₂(DA-bpy)]³⁺. Replacement of a strong donor ligand LL by a poor donor bpy (better acceptor) provides a channel for the draining of the excess charge density building in the metal center. The draining of the excess charge coming from the donor by the acceptor ligand can be detected from the relative shift of the oxidation potentials. In the specific case displayed in Figure 5, it can be noted that between Ru(DA-bpy)₃³⁺ and [Ru(bpy)₂-(DA-bpy)]³⁺, the t_{2g} level has moved down by ≈ 0.75 V when the donor $d\pi$ -level has moved down only by 0.35 V.

The derived estimates on the energy level (π) of the donor shed light on the extent of mixing of the metal and ligand orbitals back-donation and also explain the red-shifted nature of the LMCT transition in the mixed ligand complexes. In [Ru(bpy)₂-(DMA-bpy)]3+, for example, a shift of 0.75 V in the acceptor level, the donor π -level moved down only by ca. 0.35 V. Similar $d\pi - \pi^*$ mixing has been noted earlier in the MLCT transition of the Ru(II) complexes. In a series of complexes of the type [Ru- $(LL)_2(LL')$], where LL' is a better electron donor than LL, $\geq 35\%$ of the increased charge density at the Ru center is transferred to the acceptor ligand (bpy) via mixing of the $d\pi - \pi^*$ orbitals. Recently we showed an example of this type where LL = dcbpy. The extent of mixing can be estimated from the shift in the MLCT transition for a given shift in the oxidation potential, E_{ox} . In the present case, if the donor π -level had remained at the same level as in the trischelate (+2.40 V), the energy of the LMCT transition would be much smaller ($\approx 1.15 \text{ V}$). The shifts are less pronounced in the mono-bpy complexes, and the overall behavior is an intermediate one.

Sutton and Taube in their spectral studies 10a of [(NH₃)₅(4-NH₂-py)Rul³⁺ assigned the LMCT absorption as originating in the HOMO of the ligand containing the lone pair of electrons of the amine nitrogen. This was based on two observations, viz., the disappearance of the CT absorption upon protonation of the amine and absence of any absorption in the visible region in the pyridine complexes of Ru(III). In the present case moderately intense LMCT transitions are observed in cases of bipyridine derivatives where the substituents carry a lone pair of electrons (methoxy or amino). Thus any role of the lone pair of electrons on the stabilization of charges at the metal center cannot be ruled out.

Intensities of LMCT Transitions. Qualitatively the intensity of the LMCT transition increases in intensity with increasing electron-donating capacity of the donor ligands. The intensity of LMCT transitions is directly related to the electric dipole strength associated with the electronic transition. Experimentally, the oscillator strength f of the transition can be estimated using the relation

$$f = 4.6 \times 10^{-9} \bar{\nu}_{1/2} \epsilon_{\text{max}} \tag{1}$$

where $\bar{\nu}_{1/2}$ is the observed bandwidth in cm⁻¹ at one-half band height and ϵ_{max} is the maximum extinction coefficient in M⁻¹ cm⁻¹. Bandwidth values at half-height for various bands are typically in the range 1700–2000 cm⁻¹. Using the calculated values of bandwidth and associated ϵ values listed in Table III the following values of oscillator strength (f) can be calculated: [Ru(DMA-bpy)₃]³⁺0.046; [Ru(DM-bpy)₃]³⁺0.040; [Ru(DOH-phen)₂(bpy)]³⁺0.034; [Ru(DMO-bpy)₃]³⁺0.058; [Ru(bpy)₂(DA-bpy)]³⁺0.032; [Ru(bpy)₂(DMO-bpy)]³⁺0.001 68; [Ru(DM-bpy)₃]³⁺0.0037; [Ru(bpy)₃]³⁺0.0058. The decreasing values of f with decreasing donor strength is consistent with the expectations for ligand-to-metal charge-transfer transitions.

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