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Ligand to Metal Charge Transfer Transitions in Ru(III) and Os(III) Complexes of Substituted 2,2'-Bipyridines

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ABSTRACT

The variations in the energy and intensity of the low-energy LMCT transitions have been examined in the complexes $[M(X_2\text{-bpy})_3]^{3+}$ and $[M(bpy)_n(X_2\text{-bpy})_{3-n}]^{3+}$ (M = Ru or Os, X = Me, OMe, NH_2 and NMe_2). In the homo tris-chelates the energy of the low-energy LMCT transition falls within a narrow range of 1.80 ± 0.1V for Ru(III) and 2.20 ± 0.1 V for Os(III). The LMCT transition occurs at much lower energy in mixed ligand complexes. A quantitative analysis as a function of donor strength and Hammett substituent constants is presented.

INTRODUCTION

Charge Transfer (CT) transitions account for the intense color and photoredox reactivity in transition metal complexes [1]. In polypyridine complexes of Ru(II) and Os(II), for example, absorption in the visible light region is mainly due to metal-to-ligand charge transfer (MLCT) $[(d_\pi^6) \rightarrow (d_\pi^5)(\pi_L^{*1})]$. The emissive and long-lived nature in fluid solution of these MLCT excited states allowed extensive quantitative studies on the properties of these CT transitions. The oxidized M(III) form (also octahedral, low spin) in general show ligand-to-metal ($\pi_L \rightarrow t_{2g}^5$) charge transfer (LMCT) transitions in the visible light region. Much less is known on these LMCT states, possibly due to their very weak intensities ($\varepsilon \leq 500$ $M^{-1}cm^{-1}$) in the widely studied complexes $Ru(bpy)_3^{3+}$, $Os(bpy)_3^{3+}$ and

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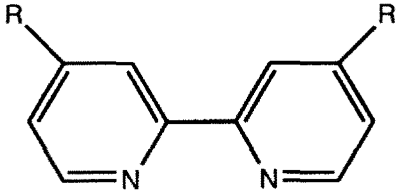
their non-emissive nature. Two key investigations of electronic spectra are those of Bryant and Ferguson [2] and of Kober [3].

As part of our studies on the use of polypyridine complexes as redox mediators in biosensors [4], we examined a number of complexes of the type $M(LL)_3$ and $M(LL)_2(LL')$ where M = Ru, Os and LL, LL' are 2,2'-bpy-based ligands with electron donor substituents at the 4,4'-position:



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

R = H (bpy)
R = Me (DM-bpy)
R = OMe (DMO-bpy)
R = NH_2 (DA-bpy)
R = NMe_2 (DMA-bpy)

Low energy LMCT transitions are favoured when the metal is oxidizing and the ligand reducing. For this reason, above complexes appeared to be ideal candidates to probe LMCT transitions. These complexes with donor substituents at the 4,4' position of 2,2'-bipyridine ligand show 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!). The properties of low energy LMCT bands have been examined by a systematic tuning of the donor strength of the bipyridine ligand using different substituents (see structures shown above). 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 are presented.

RESULTS

Chemical oxidation of complexes such as $[Ru(DA\text{-}bpy)_3]$ and $[Ru(bpy)_2(DA\text{-}bpy)]$ using oxidants such as bromine or Ce(IV) leads to disappearence of the MLCT bands and appearence of new bands in the red to near IR region. Comparison of molar absorbances show clearly that the LMCT band in these complexes with donor ligands has gained considerable intensity as compared that in the parent bpy complex, $M(bpy)_3^{3+}$. In all Ru and Os-complexes, the LMCT transition occurs at much lower energy in mixed ligand complexes as compared to the homo-

TABLE 1
Data on the low-energy absorption bands and redox potentials of Ru(III) and Os(III) complexes.

Complex	σ_p^+	E_{ox} (V)	LL-M(III) CT λ_{max}(nm) &ε($M^{-1}cm^{-1}$)	
$Ru(DMA\text{-}bpy)_3$	-1.7	+0.15	683(5820)	580(4365)
$Ru(DA\text{-}bpy)_3$	-1.3	+0.35	653(4390)	526(3160)
$Ru(DA\text{-}bpy)_2(bpy)$	-0.87	+0.60	725(4020)	594(4130)
$Ru(DMO\text{-}bpy)_3$	-0.78	+0.80	730(5150)	565(3150)
$Ru(DA\text{-}bpy)(bpy)_2$	-0.43	+0.95	746(3410)	596(2860)
$Ru(DMO\text{-}bpy)(bpy)_2$	-0.26	+1.05	841(2160)	690(560)
$Ru(DM\text{-}bpy)_3$	-0.31	+1.10	642(480)	555(250)
$Ru(bpy)_3$	0	+1.26	675(750)	
$Os(DMA\text{-}bpy)_3$	-1.7	-0.16	590(6290)	513(5705)
$Os(DA\text{-}bpy)_3$	-1.3	-0.11	527(5350)	465(5795)
$Os(DMA\text{-}bpy)_2(DM\text{-}bpy)$	-1.23	+0.10	648(5210)	562(6510)
$Os(DMA\text{-}bpy)_2(bpy)$	-1.10	+0.15	666(4850)	565(4565)
$Os(DA\text{-}bpy)_2(DMbpy)$	-0.97	+0.25	586(3210)	508((3700)
$Os(DMO\text{-}bpy)_3$	-0.78	+0.39	430(4100)	
$Os(DM\text{-}bpy)_2(DA\text{-}bpy)$	-0.64	+0.40	596(3830)	508(3480)
$Os(DM\text{-}bpy)_3$	-0.31	+0.60	536(603)	
$Os(bpy)_3$	0	+0.80	563(585)	

tris chelates. The charge transfer nature of the new absorption bands in the visible region has been established from their solvent dependence.

Redox potentials for the oxidation M(II) → M(III) were determined in acetonitrile or DMF by cyclic voltammetry. **Table 1** summarizes data on the low energy LMCT bands and redox potentials measured in this work. The electron-donor substituents increase the charge density at the metal center and this can be noted from the ease of oxidation. Bpy-complexes of Ru(II) and Os(II) complexes with strong donor ligands such as $-NH_2$ or $-NMe_2$ have $E_{3+/2+} \leq 0.35$ V and are readily oxidized by molecular oxygen. The E_{ox} values depend on the type and the number of donor ligands present. With respect to $M(bpy)_3$, 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 1.10V.

It may be noted that, in mixed ligand complexes of the type $[M(bpy)_n(LL)_{3-n}]$, the MLCT transition involves the acceptor ligand (bpy). The LMCT transition on the contrary involves the electron-rich, substituted bpy ligand LL. Examination of the data in Table 1 reveals useful trends in the energy and intensities of the LMCT transitions: i) The lowest energy LMCT transition of the tris-chelates is observed within a narrow range of 1.80 ± 0.1 eV for Ru(III) and 2.20 ± 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 homo tris chelates. This can be seen clearly in the absorption spectra shown in figure 1; 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 $Ru(bpy)_3{}^{2+}$ and $Ru(bpz)_3{}^{2+}$ complexes. In the latter complex, 0.5V anodic shift of the E_{ox} is accompanied by similar shifts in the first reduction potential.

DISCUSSION

Ligand-to-metal charge transfer involve electronic transitions between donor orbitals that are largely π(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 π(X-bpy) orbitals is enhanced and this effect is transmitted to the metal $d\pi$-orbitals by via $d\pi$-π(LL) mixing. The oxidation potential data shows that there is a corresponding ease of oxidation of the metal center from +2 to +3 state. The E_{ox} values can be varied systematically by $\approx$1.0V by using different substituted bpy ligands with donor groups ranging from X = NMe_2 to H. In tris-chelates the shift on the $d\pi$-orbitals is nearly the same as in the π-orbitals with the result that LMCT transitions are nearly iso-energetic.

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[5]. 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)]. Hammett substituent constant σ_p+ can be used as a measure of the relative donor strength of the substituted bpy ligand. In our correlations $\sigma_p{}^+$ values have been used instead of σ_p, for the latter values are more applicable for the cases where the substituent group interacts with the developing positive charge.

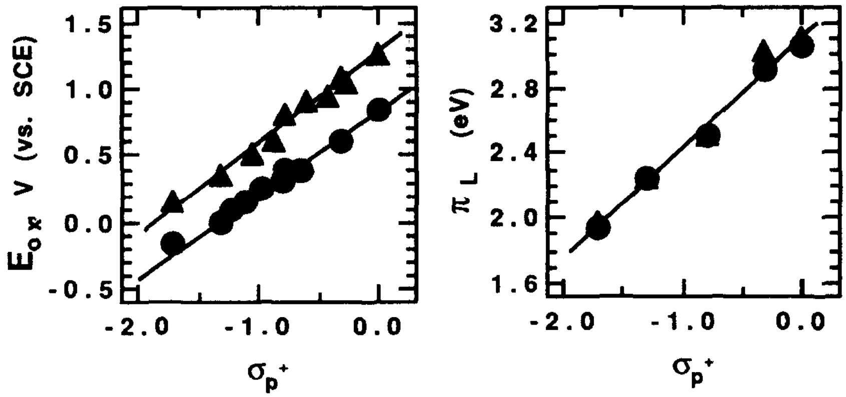


Fig.1 left: Dependence of the first oxidation potential with Hammett substituent constant σ_p+ for a series of substituted bpy-complexes of Ru(III) (triangles) and Os(III) (circles). right: Variation of the estimated energy level of HOMO of substituted bpy with σ_p+ in the Ru (triangles) and Os (circles).

Figure 1 (left) 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: $\sigma^+_{eff} = [\, n\, \sigma^+_{LL} + (3\text{-}n)\, \sigma^+_{LL'}] / 3$).

The energy of the donor level (π_L) in the Ru and Os complexes is not directly accessible. Since LMCT transition corresponds to promotion of an electron from the ligand π_L level to the partially filled t_{2g} level of the metal, the former can be estimated using the the energy of the LMCT transition and experimentally measured E_{ox} values of the respective tris-chelates, $M(LL)_3^{3+}$. 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. Figure 1 (right) shows that the dependence of the ligand π_L level with the substituent constant σ^+. For a given donor ligand, the estimated π_L value for the Ru and Os complexes differ only by ± 50 mV. As expected, the ligand π_L level shifts linearly with increasing donor strength of the substituted bpy ligand.

The lowering of the LMCT energy in mixed ligand complexes is caused by dπ-π* mixing and back-bonding effects. In terms of energies of donor and acceptor levels, the lower energy of the CT transition is obtained due to differences in the extent of shifting of these orbitals. Quantitative analysis can be made using LMCT transition energies and related oxidation potentials. In the specific case of $Ru(DA\text{-}bpy)_3^{3+}$ and $[Ru(bpy)_2(DA\text{-}bpy)]^{3+}$, the t_{2g} level has moved down by ≈ 0.75V when the donor dπ-level has moved down only by 0.35V. 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.

Similar dπ-π* mixing has been noted earlier [6] 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, ≥ 35% of the increased charge density at the Ru-center is transferred to the acceptor ligand (bpy) via mixing of the dπ-π* 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 tris-chelate (+ 2.40V), the energy of the LMCT transition would be much smaller (≈ 1.15V).

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