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Correlation Between Geometric Changes of the Ligands and Extinction Coefficient of the MLCT Absorption Band in Ru(II)–Diimine Complexes

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Abstract

Extended Hückel MO calculations have been performed on the 2,2′-bi-1,8-naphthyridine ligand, **1**, as a function of the dihedral angle between the two planar moieties, θ. The spectroscopic and electrochemical properties of the complexes $Ru(bpy)_2L^{2+}$, with L = **1**, **2**, **3** and **4** (where **2**, **3** and **4** are 3,3′-(methylene)$_n$-bridged derivatives of **1** with $n = 2$, 3 and 4 respectively) have been correlated to the calculated LUMO properties of **1** at varying θ. The unusual hypochromism shown by the complexes containing L = **2**, **3** and **4** is discussed in terms of current models for Ru → L localized transitions and taking into account the non-planarity of the poly-methylene bridged ligands.

Ru(II)–polypyridine complexes have been extensively investigated in view of possible applications in a number of light driven or light generating processes [1–7]. A long standing problem with this family has been the description of the lowest energy metal-to-ligand charge transfer, MLCT, state of the prototype $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine). Either ligand-localized or interligand-delocalized models have been proposed [7–9]. In complexes of the $Ru(bpy)_2L^{2+}$ type, where L is a bidentate ligand easier to reduce than bpy, localization of the excitation takes place and is based on the Ru–L chromophore [7]. On this basis, it is possible to investigate the relationships between energy and shape of the lowest unoccupied molecular orbital, LUMO, of L with (i) energy of the MLCT absorption band, (ii) energy of the emission band, and (iii) potentials for reduction of free L and $Ru(bpy)_2L^{2+}$ complexes [7, 10]. Even if some 300 complexes have been reported [7], systematic accounts on the role played by geometric and electronic factors of ligand origin on the MLCT absorption intensity (usually, the extinction coefficient, $\epsilon \geqslant 10^4$ cm^{-1} M^{-1}) are not frequently encountered in the literature [11–13].

In this study we correlate some properties of the LUMO of L with the hypochromism shown by some $Ru(bpy)_2L^{2+}$ complexes which are part of a larger family employing annelated ligands recently investigated by Thummel and coworkers [14–16] (L = **1**, **2**, **3** and **4**, where **1** is the 2,2′-bi-1,8-naphthyridine ligand and **2**, **3** and **4** are 3,3′-(methylene)$_n$-bridged derivatives of **1** with $n = 2$, 3 and 4 respectively and ϵ = 10 840, 9350, 6840, 5600 cm^{-1} M^{-1} for L = **1**, **2**, **3** and **4** respectively). Abbreviations used are binap = 2,2′-bi-naphthyridine, and i-biq = 3,3′-biisoquinoline. Figure 1 shows molecular formulae.

Table 1 collects some spectroscopic and electrochemical data. For comparison purposes, data for $Ru(i\text{-}biq)_2(bpy)^{2+}$ are also reported [19]. For this complex, the ligand involved in the first reduction and in the lowest energy MLCT transition is bpy, the MLCT states based on the i-biq ligand being very high in energy [20].

In order to obtain the LUMO properties of the (methylene)$_n$-bridged **2**, **3** and **4** ligands we have performed EHMO calculations on **1** by changing θ, the dihedral angle between the two planes of the naphthyridine fragments. A justification for this procedure relies on the fact that the methylene bridge is expected not to affect the π conjugation, but only to cause geometric changes. θ was estimated as 20°, 55° and 80° for $n = 2$, 3 and 4 respectively [14]. The results of the calculations are listed in Table 2.

As mentioned above, for mixed ligand $Ru(bpy)_2L^{2+}$ complexes with L larger than bpy, the first reduction is centered on the LUMO of L origin. As the lowest energy MLCT transition corresponds

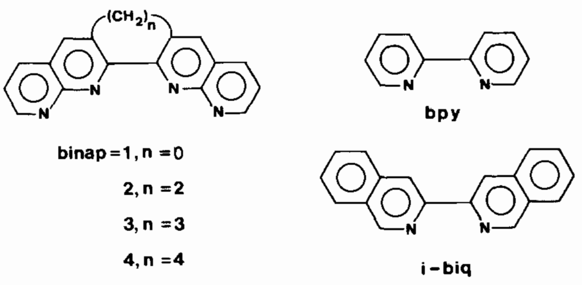

Fig. 1. Molecular formulae of the employed ligands.

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TABLE 1. Spectroscopic and Electrochemical Data for $Ru(bpy)_2L^{2+}$ Complexes[a]

L	$h\nu_{max}$[b] (ϵ) (eV)	E_{ox} (V)	E_{red}[c] (V)	$h\nu^{oo}$[d] (eV)	$\Delta E_{1/2}$[e] (eV)
1	2.16 (10840)	1.42	−0.53	2.06	1.95
2	2.15 (9350)	1.18	−0.76	2.05	1.94
3	2.18 (6840)	1.18	−0.80	2.08	1.98
4	2.20 (5600)	1.33	−0.70	2.10	2.03
bpy[f]	2.75 (11600)	1.17	−1.42	2.65	2.59

[a] From ref. 14, unless otherwise specified. Solvent CH_3CN, $T = 25$ °C. Potentials are *vs.* SCE. [b] Lowest energy absorption maximum, see text. [c] First reduction. [d] $h\nu^{oo} = h\nu_{max} - 0.1$ eV [17, 18]. [e] $\Delta E_{1/2} = e(E_{ox} - E_{red})$, see text. [f] From data for $Ru(i\text{-}biq)_2(bpy)^{2+}$ [19], see text.

TABLE 2. Calculated Properties of the LUMO for binap Ligand

L, θ[a]	E_{LUMO} (eV)	$a^*_{N,calc}$	R_{ML} (Å)
1, 0	−10.40	0.312	3.99
1, 36	−10.29	0.273	4.04
1, 76	−10.02	0.169	4.21
1, 86	−9.95	0.141	4.27
bpy, 0	−9.71	0.440	3.26

[a] Dihedral angle between the planes of the molecular moieties, see text.

to electron promotion from a metal centered orbital to the LUMO, optical energies are expected to be linearly related to redox energies, $\Delta E_{1/2} = e(E_{ox} - E_{red})$ [7], where e is the electron charge and E_{ox} and E_{red} are the first oxidation and reduction potentials respectively. Figure 2 shows that such expectation is fulfilled for the complexes taken into account, providing evidence for the validity of the approach based on a localized Ru–L fragment.

Figure 3 shows a MO energy level diagram drawn according to the results of Table 1 and Fig. 2 and consistent with symmetry based interaction schemes, eqns. (1) and (2)

$$h\nu^{oo} = \Delta_{0j} + 2X \tag{1}$$

$$\Delta_{0j} = \Delta E_{1/2} - X \tag{2}$$

where the spectroscopic energy $h\nu^{oo} = h\nu_{max} - 0.1$ eV [17, 18] and Δ_{0j} is the energy separation between non-interacting orbitals.

According to current theories for CT transitions [11, 12, 21], absorption intensities (Table 1) and L structure can be related as follows. The transition moment, μ, for a CT transition localized on a Ru–L unit is due to a 'transfer term' [11, 21]

$$\mu = -(B_{0j}R_{ML}e)/E_{0j} \tag{3}$$

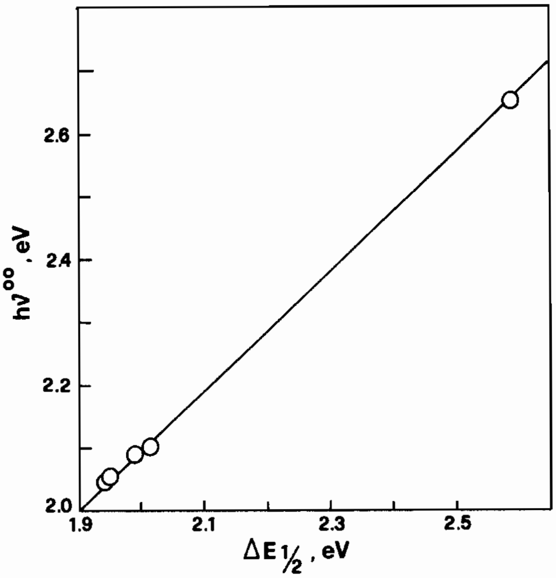

Fig. 2. Correlation between optical (absorption) and redox energies. Regression analysis gave $r = 0.998$, slope = 0.93, and intercept = 0.23 eV.

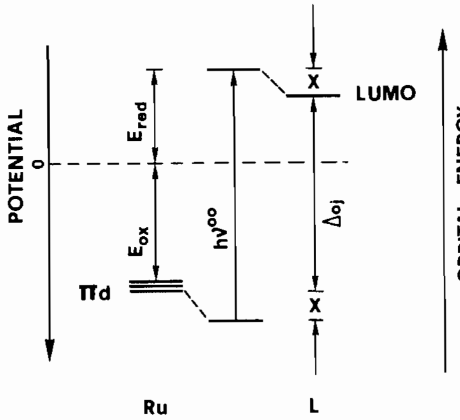

Fig. 3. Molecular orbital diagram depicting the relation between optical and electrochemical processes, see text. The interaction leading to πd → LUMO optical transfer of charge involves orbitals of the same symmetry [11].

where B_{0j} and E_{0j} are the resonance integral and the separation energy, respectively, between the zero-order ground state ψ_0 and excited state ψ_j, and R_{ML} is the distance between the donor and acceptor sites. As an approximation we will use $E_{0j} = \Delta_{0j}$. For the lowest energy MLCT transition of a Ru–L chromophore and assuming that the Ru–L interaction only involves the chelating N, one obtains [11, 21]

$$B_{0j} = a^*_N\beta_1 \tag{4}$$

where a^*_N is the N contribution to the L based LUMO and [11, 21]

TABLE 3. Parameters Derived on the Basis of the Model for CT Transitions Localized on the Ru–L Fragment

L	μ^a (eÅ)	X^b (eV)	$a^*_{N,exp}$ ^{c}
1	0.813	0.11	0.290
2	0.754	0.11	0.263
3	0.643	0.10	0.221
4	0.577	0.07	0.204
bpy^d	0.743		0.440

[a] From $\mu = (f/[\nu_{max}\ 1.085 \times 10^{-5}])^{1/2}$ and the oscillator strength $f = 4.6 \times 10^{-9}\ (\epsilon)(\nu_{1/2})$, with ν expressed in cm^{-1}. Spectroscopic data from ref. 14 ($\nu_{1/2}$ was taken as 2500 cm^{-1} in each case). [b] From eqns. (1) and (2) of the text. [c] From eqn. (5) of the text. [d] From data for Ru(i-biq)$_2$(bpy)$^{2+}$ [19], see text.

$$\mu = -(2^{1/2} a^*_N \beta_1 R_{ML} e)/\Delta_{0j} \qquad (5)$$

In eqn. (5), $\beta_1 = \langle \pi d|H|p_N\rangle$ is the resonance integral between πd and p_N atomic orbitals.

Table 3 collects μ, X, and $a^*_{N,exp}$ parameters as derived from the spectroscopic data of Table 1 or evaluated according to eqns. (1)–(5). β_1 was taken as 7400 cm^{-1}, see below. R_{ML} was calculated assuming Ru–N distances of 2.05 Å [22]. As one can see, the changes of $a^*_{N,exp}$ for L = 1, 2, 3 and 4 parallel those in absorption intensity (ϵ) for the lowest MLCT band of the related Ru(bpy)$_2$L^{2+} complexes.

Figure 4 shows the θ dependence of $a^*_{N,exp}$ and $a^*_{N,calc}$. As expected on the basis of the model for the localized Ru–L chromophore, both the series of independently derived a^*_N coefficients follow the same dependence on θ. One concludes that for the examined complexes, the geometric changes of L affect the amount of mixing between metal centered and ligand centered orbitals. In the frame of the CT theories [11, 12, 21] referred to, the reported hypochromism of the Ru(bpy)$_2$L^{2+} complexes examined appears directly correlated to a reduced transfer of electronic charge from the Ru(II) center to L.

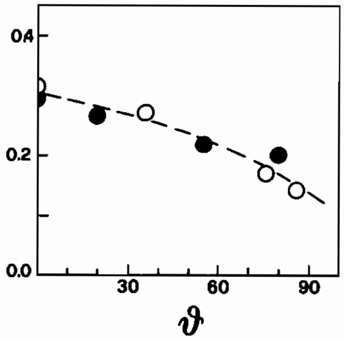

Fig. 4. Dependence of the N atomic coefficients, $a^*_{N,calc}$ (○) and $a^*_{N,exp}$ (●), on the dihedral angle, θ, between the two planar halves of L. The dashed line is only drawn for comparison purposes.

Details of Calculations

A standard EH program (QCPE No. 344) was used. Bond lengths were taken as 1.36 and 1.49 Å for the C–C distances in the aromatic ring and single bond respectively. The planar L were taken to lie on the yz plane, the z direction bisecting the N–Ru–N bite angle. The changes of θ were obtained by allowing disrotatory movements (by $\theta/2$) of the two molecular moieties of binap, with respect to the yz plane. For all ligands examined, the LUMO exhibited b_1 symmetry, under C_{2v} description, as identified on the basis of the p_x atomic contributions of the chelating N atoms [11, 12]. R_{ML} distances were calculated considering that the promoted electron spreads on the backbone of L according to the squared atomic coefficient for the LUMO. β_1 was estimated according to [21]

$$h\nu^{00} = \Delta_{0j} + 2(a^*_N\beta_1)^2/\Delta_{0j} \qquad (6)$$

We chose $\beta_1 = 7400$ cm^{-1} in order to obtain consistency with the data for Ru(i-biq)$_2$(bpy)$^{2+}$, *i.e.* for the Ru–bpy chromophore [19]. Literature values are $\beta_1 = 7540$, 6300 and 7780 cm^{-1} for L = pyrimidine, pyridine and pyrazine, respectively [21].

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