Contribution from the Istituto FRAE-CNR, Bologna, Italy, Dipartimento Chimico "G. Ciamician", University of Bologna, Bologna, Italy, and Institute for Inorganic Chemistry, University of Fribourg, Fribourg, Switzerland

Influence of the Ligand Structure on the Electrochemical and Spectroscopic Properties of Ruthenium(II)–Polypyridine Complexes

F. Barigelletti,*[1a] A. Juris,[1a,b] V. Balzani,[1a,b] P. Belser,[1c] and A. von Zelewsky[1c]

Extended Hückel molecular orbital (EHMO) calculations on 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), and other unsubstituted polypyridine-type molecules have been performed to study the effect of the ligand structure on the spectroscopic and electrochemical properties of Ru(II)–polypyridine complexes. The obtained LUMO energies have been found to correlate with the first reduction potential of LL' and with the first reduction potentials of $Ru(LL')_3^{2+}$ or $Ru(LL)_2(LL')^{2+}$ complexes, where LL' is a ligand easier to reduce than LL. Correlations between optical and electrochemical data of the same complexes have also been examined. Complexes containing LL' = taphen, DP or i-biq (taphen = dipyrido[3,2-c:2',3'-e]pyridazine, DP = dipyrido-[3,2-a:2',3'-c]phenazine, i-biq = 3,3'-biisoquinoline) show an anomalous electrochemical and/or spectroscopic behavior. Possible reasons for such anomalies are discussed.

Introduction

There is currently a great interest in developing correlations[2–6] between optical and electrochemical properties of the Ru(II)–polypyridine complexes,[7–10] which can be employed as sensitizers in a number of light-driven[11–14] or light-generating[15–17] processes. Such correlations are most useful because they offer the opportunity to obtain absorption and emission energies from electrochemical potentials and vice versa[2–6,10,18] and may also reveal details concerning the solvation and reorganization energies.[3c] For the Ru(II)–polypyridine complexes, the basis for the correlations lies on the fact that the same metal-centered and ligand-centered orbitals that are involved in the metal-to-ligand charge-transfer (MLCT) transition are also involved in the oxidation and reduction processes. More specifically, the lowest energy Ru → ligand transition involves the promotion of an electron from a metal-centered π_M orbital to the lowest antibonding ("spatially isolated")[19] ligand-centered π^*_L orbital, which resembles the lowest π^* orbital of the free ligand.

In some cases MO calculations on the free ligands have been employed to elucidate the substituent effect on the redox properties of Ru(II) complexes containing bpy-substituted (bpy = 2,2'-bipyridine) ligands, and the electron-withdrawing or -donating ability of the substituent has been related to the calculated electron density of the LUMO at the substituent position.[20] Calculations concerning large changes in the ligand structure, however, have seldom been used for correlation purposes.[21,22] One expects, of course, that the more extended the ligand molecular backbone is the closer the ligand-centered LUMO and the metal-centered HOMO will be and the lower the energy of the corresponding MLCT transition energy will be.[23,24]

In this paper we will consider correlations concerning homoleptic $Ru(LL')_3^{2+}$ and heteroleptic $Ru(LL)_2(LL')^{2+}$ complexes, where LL' is a ligand easier to reduce than LL. For such complexes the attention can be focused on a Ru–LL' unit of C_{2v} symmetry. This is actually the symmetry of the Ru–LL' fragment that is present in the $Ru(LL)_2(LL')^{2+}$ complexes and is also an appropriate description for the monoreduced or excited $Ru(LL')_3^{2+}$ species because both processes involve population of a π^* orbital localized in a single LL' ligand.[4,5,10,19,25] A schematic MO diagram showing the orbitals relevant to our discussion is shown in Figure 1. The splitting of the octahedral $\pi_M(t_{2g})$ orbitals is not shown since a different ordering of the metal-centered orbitals may occur depending on the relative strengths of the interactions with the $\pi^*(LL')$ and $\pi^*(LL)$ orbitals of appropriate symmetry.

We have performed EHMO calculations on the ligands of Figure 2 and examined the correlations between the LL' LUMO energy and the electrochemical and spectroscopic properties of complexes of the type $Ru(LL')_3^{2+}$ and $Ru(LL)_2(LL')^{2+}$. The ligands taken into account are 3,3'-biisoquinoline (i-biq), 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), 4,4'-diphenyl-2,2'-bipyridine (4,4'-dpb), 2,2'-bipyrimidine (bpym), 2-(2-pyridyl)quinoline (pq), 2,2'-biquinoline (biq), 2,2'-bipyrazine (bpz), dipyrido[3,2-a:2',3'-c]phenazine (DP), and dipyrido[3,2-c:2',3'-e]pyridazine (taphen).

Calculations

A standard EH program (QCPE No. 344) has been employed for the EHMO calculations. Bond lengths in the aromatic rings and single C–C bond lengths were taken to be 1.36 and 1.49 Å, respectively. By analogy with the excited-state conformation of biphenyl,[26] the structure of the

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Table I. Reduction Potential and Calculated Properties of the Lowest Unoccupied Molecular Orbital (LUMO) and Second Lowest Unoccupied Molecular Orbital (SLUMO) of the Free Ligands

	$E_{1/2}(LL')$,[a] V	LUMO			Q,[b] eV	SLUMO		
ligand		energy, eV	(p_N, p_N)[c]	sym		energy, eV	(p_N, p_N)[c]	sym
(a) i-biq	−2.20[d]	−9.56	(0.35, 0.35)	ψ	4.03	−9.51	(0.31, −0.31)	χ
(b) bpy	−2.22[e]	−9.71	(0.44, 0.44)	ψ	4.89	−8.86	(0.37, −0.37)	χ
(c) phen	−2.04[f]	−9.77	(0.44, 0.44)	ψ	4.90	−9.47	(0.26, −0.26)	χ
(d) 4,4'-dpb	−2.06[g]	−9.79	(0.41, 0.41)	ψ	4.44	−9.17	(0.31, −0.31)	χ
(e) bpym	−1.80[f]	−9.94	(0.35, 0.35)	ψ	4.92	−9.46	(0.30, 0.30)	ψ
(f) pq	−1.94[g]	−10.01	(0.44, 0.34)	ψ	4.55	−9.02	(0.14, −0.47)	χ
(g) biq	−1.74[e]	−10.19	(0.39, 0.39)	ψ	4.50	−9.31	(0.25, −0.25)	χ
(h) bpz	−1.70[f]	−10.47	(0.45, 0.45)	ψ	4.77	−9.91	(0.36, −0.36)	χ
(i) DP	−1.18[h]	−10.66	(0.10, 0.10)	ψ	2.70	−9.76	(0.44, 0.44)	ψ
(j) taphen	−1.26[i]	−10.78	(0.12, −0.12)	χ	3.50	−9.79	(0.44, 0.44)	ψ

[a] Reduction potential, room-temperature data in acetonitrile unless otherwise specified. Uncertainties (±30 mV) derive from data obtained by taking the Ru(bpy)$_3^{2+/+}$ couple as internal reference in the original papers. [b] Coulombic contribution obtained by electron promotion from metal to the LUMO, see text. [c] MO atomic coefficients on chelating N positions. [d] Reference 34. [e] Belser, P.; von Zelewsky, A. *Helv. Chim. Acta* **1980**, *63*, 1675. [f] Reference 32. [g] Reference 4, extrapolated from data at −54 °C. [h] Reference 35, irreversible, in dimethylformamide. [i] Reference 29.
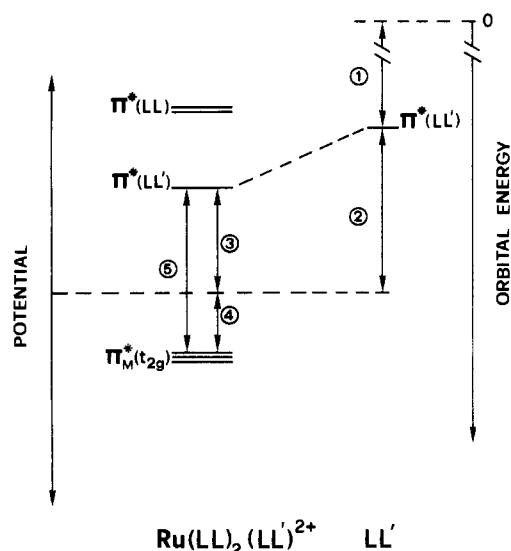

Ru(LL)$_2$(LL')$^{2+}$ LL'

Figure 1. Orbital diagram showing in a schematic way the basis for the energy correlations between the calculated energy of the LUMO of LL', the electrochemical properties of the free ligand LL', and the spectroscopic and electrochemical properties of Ru(LL)$_2$(LL')$^{2+}$ complex: (1) Calculated LUMO energy for the free LL' ligand; (2–4) energy differences related to the reduction potential of the free LL' ligand, the reduction potential of the LL' ligand in the complex, and the oxidation potential of the complex, respectively; (5) energy difference related to the lowest energy MLCT transition and to the redox energy. The splitting of the $\pi_M(t_{2g})$ orbital caused by the interaction with the LL and LL' ligand orbitals is not shown. For more details, see text.

Figure 2. Structural formulas of the ligands examined.

reduced species of 4,4'-dpb has been taken with the phenyl rings coplanar with the bpy core. The Coulombic interaction energy Q, resulting from the interaction between the positive hole on the metal and the electron promoted to the LUMO of LL', was calculated according to eq 1, where

$$Q = e\sum_i q_i/r_i\epsilon \tag{1}$$

q_i is the fractional charge on atom i of the ligand obtained by hypothetical transfer of unit charge, r_i is the distance between Ru and the ith atom of the ligand backbone (the Ru–N bond length has been taken as 2.05 Å[27]), and ϵ is the dielectric constant, taken equal to 1 as expected for a gas phase or, approximately, for an intramolecular electron transfer.[28]

Extended Hückel calculations on the bpy,[24] phen,[24] and biq[29] ligands performed by other authors are in substantial agreement with our results. Hückel calculations performed by Ernst and Kaim[22] for the bpz and bpym ligands gave slightly different energy values from those reported in this work.
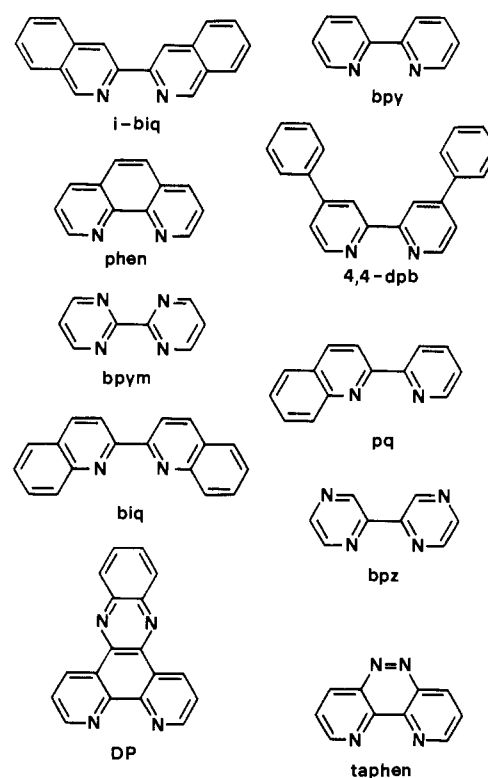
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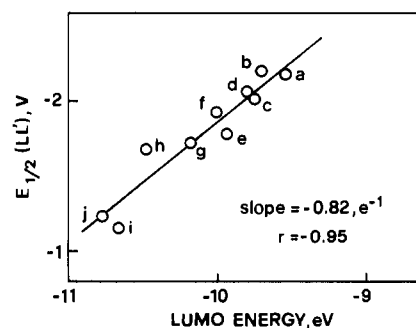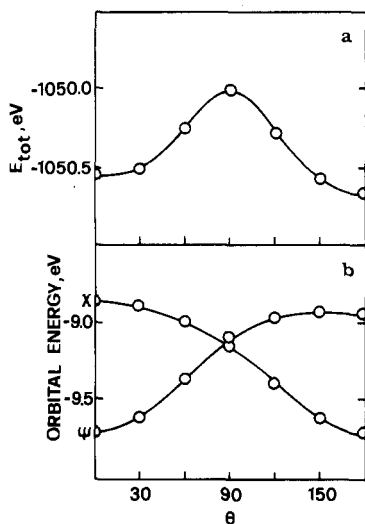

Figure 3. Correlation between the reduction potential of the free ligand LL' and its calculated LUMO energy. The ligands are labeled as in Table I.

Results and Discussion

Correlations Concerning the Free Ligand. Table I reports the reduction potentials and the calculated energies of the LUMO and of the SLUMO (second lowest unoccupied molecular orbital) of the ligands shown in Figure 2. Considering a C_{2v} symmetry for the Ru–LL' unit, the LUMO has usually $\psi(b_1)$ symmetry while

Figure 4. Energies as a function of the angle between the two molecular halves for the reduced bpy molecule (a) and the two lowest unoccupied orbitals of the bpy molecule (b).

the SLUMO has usually $\chi(a_2)$ symmetry,[30] thus providing effective interaction patterns with $d(b_1)$ and $d(a_2)$ metal orbitals, respectively.[23] The calculated LUMO energies vary over a range of more than 1 eV and the energy separation (Δ) between LUMO and SLUMO orbitals is 0.5–1.0 eV for most ligands except for i-biq ($\Delta = 0.05$ eV) and phen ($\Delta = 0.3$ eV). The atomic coefficients p_N of the LUMO on the chelating N atoms are on the order of 0.4 except for DP and taphen.

Figure 3 shows that the energy of the LUMO, E_{LUMO}, and the reduction potential of the free ligand, $E_{1/2}(LL')$, are linearly related. For those ligands that have an internal degree of freedom, the calculations have been performed for the chelating (cis planar) geometry. In principle this might be incorrect because the equilibrium geometry for the reduced species is generally not known and the ground state of the free ligand is known to assume a trans geometry.[31] However, the energy changes with ϑ (the angle between the two molecular halves: $\vartheta = 0°$ corresponds to cis geometry) for monoreduced bpy (Figure 4) and i-biq showed that although the LUMO orbital can be different for the cis or trans conformation, the values of the energy minima for $\vartheta = 0°$ or $\vartheta = 180°$ are almost equal (their difference is actually on the order of the data scattering in Figure 3).

Correlation Concerning the Ru(II) Complexes. Table II reports the electrochemical and spectroscopic data for $Ru(LL')_3{}^{2+}$ or $Ru(LL)_2(LL')^{2+}$ complexes that are labeled as the corresponding LL' free ligands of Table I. The complexes have been selected in such a way that the interligand steric hindrance is minimized. To do that, when LL' is a large-sized ligand only mixed-ligand complexes containing smaller LL ligands are taken into account. This allows us (i) to keep the ligand field strength approximately constant, (ii) to maintain the metal-centered σ^* orbitals enough high in energy to avoid their involvement in the reduction process, and (iii) to deal with Ru–LL' fragments featuring approximately the same Ru–N bond length.

Under the reduced C_{2v} symmetry, the lowest energy MLCT transition is conveniently described in terms of a single configuration, d → LUMO, provided that the energy separation Δ between LUMO and SLUMO is large enough. For instance, this is the case for $Ru(bpy)_3{}^{2+}$ ($\Delta = 0.85$ eV, Table I).[24] From the data of Table I it seems likely that the lowest energy MLCT transitions for the complexes of Table II can be described by a single configuration except for that of $Ru(i\text{-}biq)_3{}^{2+}$ ($\Delta = 0.05$ eV). Under such conditions, it can be shown[2-5,10,18,29,32] that the energy

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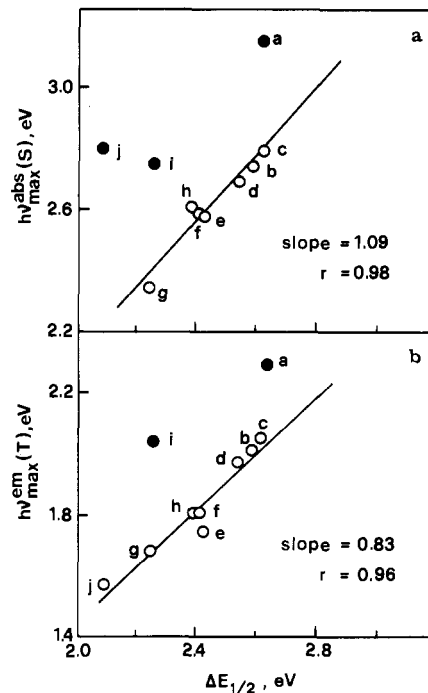

Figure 5. Correlations between the redox energy $\Delta E_{1/2}$ and the energy of the absorption (a) and emission (b) maxima for the complexes listed in Table II. Full points were not employed for the regression analysis.
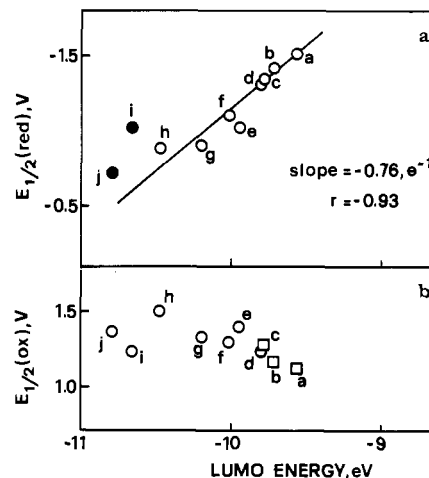

Figure 6. Correlation between the calculated LUMO energy of the free LL' ligand and the reduction (a) or oxidation (b) potentials for the complexes listed in Table II. Full points were not employed for the regression analysis.

of the absorption (to the singlet) and emission (from the triplet) maxima of the MLCT transition involving the $\pi^*(LL')$ LUMO are given by eq 2 and 3, where $\Delta E_{1/2} = e[E_{1/2}(ox) - E_{1/2}(red)]$,

$$h\nu_{max}{}^{abs}(S) = \Delta E_{1/2} + A \tag{2}$$

$$h\nu_{max}{}^{em}(T) = \Delta E_{1/2} + B \tag{3}$$

$E_{1/2}(ox)$ and $E_{1/2}(red)$ are the oxidation and reduction potentials of the complex, and A and B include terms that take into account solvation energies, inner- and outer-sphere barriers, and Coulombic energies. The Coulombic term Q, i.e. the stabilization electrostatic interaction between the positive hole and the electron distributed on the molecular framework of the receptor ligand, is particularly important because it can be largely different for different ligands. The calculated values of Q for the hypothetical transfer of a unit charge from the metal to the LUMO of the LL' ligand are shown in Table I.

The plots of $h\nu_{max}{}^{abs}(S)$ and $h\nu_{max}{}^{em}(T)$ vs $\Delta E_{1/2}$ are shown in Figure 5. As one can see, the expected linear correlation is

Table II. Redox Potentials and Spectroscopic Properties of the Ru(II) Complexes at Room-Temperature in Acetonitrile

complex	$E_{1/2}$(ox),[a] V	$E_{1/2}$(red),[a] V	$\Delta E_{1/2}$,[b] eV	$h\nu_{max}^{abs}(S)^c$		$h\nu_{max}^{em}(T)^d$		ref
				λ, nm	ν, eV	λ, nm	ν, eV	
(a) Ru(i-biq)$_3$$^{2+}$	1.12	−1.51[e]	2.63	392	3.16	540	2.29	7
(b) Ru(i-biq)$_2$(bpy)$^{2+}$	1.17	−1.42	2.59	450	2.75	615	2.01	7
(c) Ru(phen)$_3$$^{2+}$	1.27	−1.35	2.62	442	2.80	604	2.05	32
(d) Ru(bpy)$_2$(4,4′-dpb)$^{2+}$	1.23	−1.31	2.54	458	2.70	628	1.97	4
(e) Ru(bpy)$_2$(bpym)$^{2+}$	1.40	−1.02	2.42	480	2.58	710	1.74	5b
(f) Ru(bpy)$_2$(pq)$^{2+}$	1.30	−1.11	2.41	478	2.58	700	1.77	7
(g) Ru(bpy)$_2$(biq)$^{2+}$	1.33	−0.91	2.24	526	2.35	742	1.67	7
(h) Ru(bpy)$_2$(bpz)$^{2+}$	1.50	−0.89	2.39	471	2.63	690	1.79	7
(i) Ru(bpy)$_2$(DP)$^{2+}$	1.24	−1.02	2.26	448	2.76	610	2.03	35
(j) Ru(bpy)$_2$(taphen)$^{2+}$	1.37	−0.72	2.09	440	2.81	788	1.57	29

[a] Oxidation and reduction potentials taken from the original works. If one takes the potentials of the Ru(bpy)$_3$$^{3+/2+}$ and Ru(bpy)$_3$$^{2+/+}$ couples given in the original papers as internal references, the uncertainty on the reported values is ±30 mV. [b] Redox energy, see text. [c] Lowest energy absorption maximum; estimated error, ±10 meV. [d] Energy of the maximum of the emission band; estimated error, ±20 meV. [e] Irreversible.
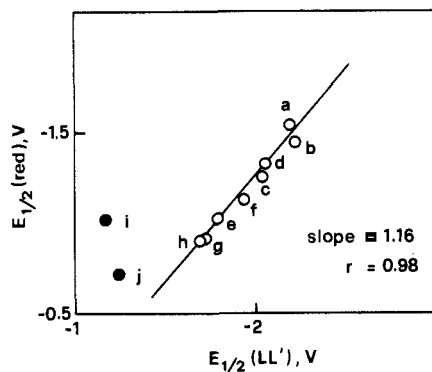

Figure 7. Correlation between the reduction potential of the free LL′ ligand (Table I) and the reduction potential of the corresponding complexes (Table II). Full points were not employed for the regression analysis.

observed in general, but there are a few dramatic exceptions.

Figure 6 shows the relation of $E_{1/2}$(red) and $E_{1/2}$(ox) for the complexes of Table II with the E_{LUMO} of the LL′ ligands reported in Table I. The linear relation of Figure 6a confirms that the accepting orbital of the complex is generally the LL′ LUMO orbital but also shows that taphen and perhaps also DP behave in an anomalous way. As far as oxidation is concerned, the LL′ LUMO energy has no clear effect (Figure 6b). Indeed, only a small effect is expected when the HOMO orbital of the complex is a d metal orbital that does not interact with the LUMO of the LL′ ligand. This is likely the case for our Ru(LL)$_2$(LL′)$^{2+}$ complexes (points d–j of Figure 6b) since the stabilization caused by the LUMO of LL′ on its symmetry-matched d orbital is expected to be larger than that caused by the LUMO of LL on the other d orbitals. A similar observation has recently been reported for some metal carbonyl complexes containing bidiazine ligands.[33]

Figure 7 shows the correlation between the reduction potential of the complexes, $E_{1/2}$(red), and the reduction potential of the corresponding LL′ ligands, $E_{1/2}$(LL′). There is again a linear correlation with a few exceptions (see below), confirming that reduction occurs to a ligand-centered orbital that resembles the LUMO of the free ligand.

As one can see, the design of new complexes with predicted redox and spectroscopic properties can be pursued on the basis of the above linear relations and of EHMO calculations on the free ligand, but much care must be exercised because of the possibility of anomalous behavior.

Anomalies. The plots of Figures 5–7 show that in general there are good correlations between spectroscopic energies, redox potentials, and calculated energies of the LL′ LUMO orbital. However, they also show that for the complexes of some ligands such correlations do not hold.

The electrochemical reduction potentials reported in Tables I and II show that in most cases the reduction potential of the free

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ligand becomes more positive by ∼0.8 V when the ligand is coordinated to the metal (see also Figure 7). Such an effect can be ascribed to the loss of negative charge by the ligand upon coordination, which occurs via σ-donation by the chelating N atoms. Assuming that the σ-donor and π-acceptor abilities (or their difference) are approximately the same for the various ligands, the lowering in energy of the LUMO orbital of a coordinated LL′ ligand will depend on the degree of its "localization" on the chelating N atoms, which acquire positive charge on coordination. The small p_N coefficients (Table I) of the taphen and DP LUMOs are expected to cause smaller positive shifts in the redox potential and can thus qualitatively account for the anomalous behavior of these two ligands in the plots of Figures 6a and 7.

This "refractory" character of the LUMOs of taphen and DP cannot account, however, for the anomalous behavior of the taphen and DP complexes in the plots of Figure 5 because both quantities correlated in these plots should depend on the properties of the coordinated ligand. It can also be noted that the i-biq complex, which behaves regularly in the plots of Figures 6a and 7, appears to be anomalous in the spectroscopic–electrochemical correlations of Figure 5. Inspection of Table I shows that the complexes that behave anomalously in Figure 5a are those which exhibit a low Coulombic interaction energy Q. This small value of Q, which is related to the extension of the ligand backbone and/or to the distribution of the electron density of the LUMO, destabilizes the MLCT excited states and thus is expected to shift the MLCT absorption to the blue. This qualitatively accounts for the fact that in Figure 5a the points related to i-biq, DP, and taphen lie above the straight line that connects the points related to the other complexes.

According to the Q values of Table I, the DP complex (point i) should be that exhibiting the most anomalous behavior. Figure 5a shows that, in fact, the point of this complex is noticeably closer to the straight line than the points of i-biq and taphen. A possible explanation may be based on the fact that the observed bands for the taphen and DP complexes involve the SLUMO orbital. This orbital lies ∼1 eV higher than LUMO in the free ligand but should have a much higher Q value than that of the LUMO because of its large localization on the chelating N atoms (see the p_N values in Table I). This implies that the SLUMO is more strongly stabilized and may become, in fact, the orbital involved in the lowest energy MLCT transition. Actually the SLUMO of DP and taphen are quite similar in energy and p_N to the LUMO of phen, so that they are expected to give rise to MLCT bands at approximately the same energy as that correspondent to the LUMO of the phen complex. As one can see from Figure 5a, the absorption maxima of the DP and taphen complexes are indeed at almost the same energy as the absorption maximum of the phen complex. The bands corresponding to the DP and taphen LUMOs could lie at comparable or higher energies, and in any case, they are expected to have lower extinction coefficients because of the smaller p_N values (and, in the case of taphen, also because of symmetry reasons). In conclusion, for the i-biq complex the orbital involved in the high-intensity absorption band is the LUMO ligand orbital, which is also involved in the reduction of the complex,

and the lack of correlation in Figure 5a is likely due to the lower stabilization energy (compared with the other complexes) for the LUMO-based MLCT state. For DP and taphen complexes, however, it seems more likely that the lack of correlation also implies a different nature of the orbitals involved in the electrochemical reduction and light absorption processes.

Concerning the correlation between emission energy and reduction potential (Figure 5b) it can be noted that the complexes of i-biq and DP behave again in an anomalous way, while the taphen complex apparently follows the linear relationship obeyed by the other complexes. The luminescence lifetime of the Ru-(i-biq)$_3$$^{2+}$ shows that the emitting excited state is largely ligand centered in character.[34] This inversion in the energy ordering between MLCT and LC levels in passing from the singlet to the triplet manifold is not unexpected because of the larger singlet–triplet splitting of the LC states. The smaller distance from the straight line of the i-biq point (compare parts a and b of Figure 5) is in agreement with the coming into play of a lower energy LC excited state.

For the DP complex, the emission is apparently CT in nature. Comparison between parts a and b of Figure 5 suggests that the same orbital (or energetically similar orbitals) is involved in the absorption and emission process. As we have seen above, the most likely explanation for the absorption properties assumes the involvement of the free ligand SLUMO, whereas excited-state absorption spectra have shown that the excited electron is largely localized on the phenazine moiety of the ligand,[35] i.e. on the LUMO orbital. The lack of correlation between emission and redox energies seems to imply that the observed luminescence does not come from the CT excited state involving the LUMO, but from a higher energy (thermally activated) excited state. A possible explanation would involve a smaller excited-state distortion

for this complex (and hence Stokes shift) due to the very extended fused-ring structure of the ligand.[36]

Figure 5b shows that the taphen complex apparently is well-behaved in the correlation between emission energy and redox potential. This is quite surprising because even if the same (LUMO) orbital is involved in the emission and reduction processes, one expects a lack of correlation as in Figures 6a and 7 because of the small Q value (Table I). We believe that a plausible explanation may be the following. The LUMO of taphen is strongly localized on the N=N bridge (Figure 2) of the molecule (the p_N values in the 5- and 6-positions are +0.56 and −0.56),[37] which implies that the reduced ligand is strongly distorted along the N$_5$–N$_6$ bond. As a consequence, in the taphen complex the minimum of the potential energy surface of the ^{3}MLCT excited state involving the LUMO should be strongly displaced compared to that of the ground state, thus decreasing the energy of the emission maximum. This apparently compensates for the expected higher emission energy due to the smaller Q value. This explanation is consistent with the results obtained for the temperature dependence of the luminescence of taphen–Ru(II) complexes discussed in a previous paper.[37]

Registry No. i-biq, 35202-46-1; bpy, 366-18-7; phen, 66-71-7; 4,4′-dpb, 6153-92-0; bpym, 34671-83-5; pq, 7491-86-3; biq, 119-91-5; bpz, 10199-00-5; DP, 19535-47-8; taphen, 653-05-4; Ru(i-biq)$_3$$^{2+}$, 82762-29-6; Ru(i-biq)$_2(bpy)^{2+}$, 89340-69-2; Ru(phen)$_3$$^{2+}$, 22873-66-1; Ru(bpy)$_2$-(4,4′-dpb)$^{2+}$, 93461-97-3; Ru(bpy)$_2$(bpym)$^{2+}$, 65013-22-1; Ru(bpy)$_2$-(pq)$^{2+}$, 74171-82-7; Ru(bpy)$_2(biq)^{2+}$, 75777-90-1; Ru(bpy)$_2(bpz)^{2+}$, 85335-53-1; Ru(bpy)$_2(DP)^{2+}$, 87564-74-7; Ru(bpy)$_2$(taphen)$^{2+}$, 98914-20-6.

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Notes

Contribution from the Department of Chemistry, Thimann Laboratories, University of California, Santa Cruz, California 95064, and Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4

Synthesis, Structure, and Properties of Tetraphenylphosphonium Tetrakis(2-mercaptopropionato)trinickelate(II), (Ph$_4$P)$_2$[Ni$_3$(SCH(CH$_3$)COO)$_4$]: A Linear Trimeric Thiolato Complex of Nickel

Steven G. Rosenfield,† Maria L. Y. Wong,‡ Douglas W. Stephan,‡ and Pradip K. Mascharak*†

Our interest in synthesis of discrete thiolato complexes of divalent nickel stems from the occurrence of a S-ligated nickel center at the active site of the Ni-containing hydrogenases.[1–7] In a previous paper,[8a] we have reported the convenient synthesis and properties of distorted tetrahedral arenethiolates of the type [Ni(SAr)$_4$]$^{2-}$. Recently, we have also reported the syntheses, structures, and spectral characteristics of two distorted octahedral

Ni(II) thiolato complexes.[9] Though attempts to model the active site of the enzyme(s) are directed toward synthesis of mononuclear nickel complexes, interest in the chemistry of nickel thiolates has resulted in multinuclear nickel–thiolato species with novel

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†University of California.
‡University of Windsor.