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A Basic Electronic Model for the Study of Optical Properties of Delocalized and Partially Localized Donor−Bridge−Acceptor Systems

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An electronic model for donor−bridge−acceptor systems is discussed for the specific cases of $[(NH_3)_5Ru\text{-pyz-}Ru(NH_3)_5]^{m+}$ and $[(NH_3)_5Ru\text{-}(4,4'\text{-bpy})\text{-}Ru(NH_3)_5]^{m+}$ (m = 4, 5, 6) as well as for their longer chain analogues. The model accounts for the optical properties observed in the near-IR−vis and provides an explanation of their dependence upon the oxidation state of the metals as well as of the effect of changing the bridging ligand. The results obtained suggest that this model contains the essential ingredients for being considered a basic minimal model for the study of electron transfer in donor−bridge−acceptor systems.

Introduction

In the past few years there has been a growing interest of chemists and physicists in molecular and polymeric materials which can be useful for optoelectronics and nonlinear optics applications. In fact, many molecular systems have proven their technological importance in the field of electronic and information technologies. These systems exhibit properties, interesting *per se*, which are also of potential technological interest:[1−3] semiconductivity, metallic behavior, superconductivity, ferromagnetism, nonlinear optical properties, electrochromism. In particular, donor−bridge−acceptor systems have been proposed as high-speed molecular switches,[4−6] electrochromic devices based on lanthanide sandwich compounds have already been realized,[7] and high-T_c superconductivity is very well-known in copper oxide-based materials.

Within this field, an interesting class of compounds is that where two or more atoms of transition metals are kept together by bridging ligands, forming a chain or, in general, a lattice. Among these is of particular interest the case of mixed-valent (MV) compounds, e.g. those in which all metallic atoms are equals but have, within the molecule, different oxidation states. In this case, the excess electron(s) present in the metallic sites having the lowest oxidation state can move along the molecule, and this gives rise to the various interesting properties reported above: in extended systems, moving electrons create a current and then we can have conductivity or superconductivity, while the existence of local spin interaction, when mediated by electronic delocalization, can give rise to ferromagnetic ordering,[8] and so on.

Researchers have been and are still puzzling with various transition metals and ligands, and a large variety of MV compounds have been synthesized and studied. Beside the papers referred to below in this article, we may cite refs 9−14. Most of the interest is focused on Ru compounds, but there are many studies on compounds with other metals and we cite here only some examples on Pt^{II}/Pt^{IV},[10] Co^{II}/Co^{III},[12] and Fe^{II}/Fe^{III} [14] compounds. In this perspective, work is in progress on Co^{III} β-ketoenolates[15] in order to study a bridged dimer[16] in which preliminary electrochemical measurements appear to indicate valence delocalization.[17]

Among the various mixed-valent compounds, of particular interest is the well-known Creutz−Taube (C−T)[18] ion (pyrazine-bridged Ru dimer). This compound has been the subject of controversy for many years, as its localized or delocalized character was uncertain. Now experiments[19−21] and theory[22] point toward its delocalized nature, and the role of vibronic interaction and electronic correlation has been also pointed out.[23,24] Longer chain analogues of the C−T ion have also been synthesized,[25] and both theoretical predictions[26,27] and experi-

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mental findings[28] seem to indicate the possibility that these compounds may act as semiconductors. Furthermore, the theoretical study of the electrochromic effect (or Stark effect) was very recently accomplished for the C−T ion,[29] and comparison with experimental results[19,30] confirms the validity of the model proposed.[24]

The results obtained in our previous work allow us to draw some conclusions on the role played by various effects in producing the observed optical properties of chains of Ru atoms bridged by pyrazine (pyz).

As far as the position and intensity of absorption bands in the near-IR−vis are concerned, they can be explained within a purely electronic picture. Essential ingredients to be considered are the electronic correlation on the metal atoms, the metal−ligand resonance integral, and the metal−ligand energy gap. The line shape and, obviously, all related observables, such as for instance the shape of the difference spectra reported in the Stark effect studies,[19,29,30] require instead the inclusion of vibrational degrees of freedom. However, the coupling of electronic and nuclear motion is not so strong to necessitate that the full vibronic problem be solved and an adiabatic approach is sufficient.[24] Therefore, the role of vibronic coupling in delocalized systems such as Ru−pyz chains appears to be simply that of causing width and asymmetry in the observed line shape.

This is not a big surprise. It is universally accepted that delocalized systems are not characterized by strong vibronic coupling. Indeed, this was also predicted by early models, such as the two-state model by Piepho, Krausz, and Schatz (PKS)[31] and its extensions.[32] These models also predict a very relevant role of vibronic interaction for partially localized MV compounds, for which the estimate of metal−metal interaction is often incorrectly determined by a misapplication of the Hush formulas,[33] which are more appropriate for fully localized systems. With the oversimplification of two-state models, which disregard the explicit role of the ligand, which is important in many cases,[22] vibronic coupling is included in the model to explain the presence of low-intensity intervalence (IT) bands in partially localized MV compounds (those also known as class II systems according to the Robin−Day classification scheme[34]).

Vibronic coupling is expected to play a relevant role in some donor−bridge−acceptor systems, especially when the coordination sphere of the metal involved is known to have vibrational frequencies that change substantially as the metal ion's oxidation state varies, such as for Co and Fe.[35] However, our point of view is that in many delocalized cases and also for partially localized systems, most of the observed optical properties, such as the optical behavior in the near-IR−vis, may be explained within a purely electronic picture, which then allows an easy understanding of the relevant transitions involved. Indeed, we will show that a proper electronic model that takes into account the effect of electronic correlation, which is an extension of the one proposed for delocalized Ru-pyz chains,[26,27] is able to reproduce the position and intensity of the observed bands in the near-IR−vis for the $[\mathrm{Ru\text{-}4,4'\text{-}bpy\text{-}Ru}]^{5+}$ and give some explanation on the differences between this compound and its delocalized companion $[\mathrm{Ru\text{-}pyz\text{-}Ru}]^{5+}$.

The aim of this paper is then to present and discuss this model and its differences with the previous PKS and Hush models, in view of its possible application to other MV compounds. We are confident that our approach is appropriate for delocalized or partially localized (i.e. class III or class II) Ru−L−Ru compounds with various bridging ligand L.[36−38]

Our goal is to construct a clear and easy theoretical description and understanding of the properties of MV compounds which can help in designing new chemical systems suitable for molecular electronics applications.

The Model

Early models proposed for studying the optical properties of MV compounds, such as the Hush[33] model and the PKS model,[31] were based on a two-state approach; the PKS model introduced the effect of vibronic interaction not explicitly considered in the Hush model. Within this approach, a MV compound is seen as a donor−acceptor (DA) couple and the electron transfer (et) process ($DA \rightarrow D^+A^-$) is thus related to the coupling (H_{ab}) between two diabatic states, one for each unit (DA and D^+A^-). Diabatic states are modeled as harmonic oscillators, and the intervalence transition (IT), observed in the near-IR−vis, is explained as the transition from the two adiabatic states obtained from the solution of the 2 × 2 secular problem in the DA and D^+A^- basis in the Hush model (see also ref 39), while it is a vibronic transition in the PKS model.

However, two-state models are often too strong a simplification. Indeed, while the et process can be intuitively viewed as a two-state process in which one electron goes from a donor (D) to an acceptor (A) moiety of a DA molecule, this does not mean that all the essential physics involved has been taken into account. For instance, for the study of et in bridged (D−B−A) systems a two-state model can be applied with success only if the bridge does not play an explicit role. When this is not verified, then the bridge must be taken into account, such as for the Ru-pyz-Ru ions[22−24] and their longer chain analogues.[26,27] In general, we may say that if the energy difference between the orbital involved in the et process of B and those of D and A is much higher than the corresponding interaction terms, then, within a perturbative approach, the bridge can be projected out giving rise to a two-state model; H_{ab} is then the effective coupling $V_{DB}V_{AB}/\Delta E_{DB}$ and $|a\rangle$ and $|b\rangle$ are thus DA and D^+A^- states, respectively (for a general reference see ref 40; for reference related to superexchange in electron transfer, see refs 41 and 42).

Very recently, work has been done in order to derive H_{ab} from quantum calculations;[43] the evidence that the two diabatic

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states are not dipole-connected (i.e. $\mu_{ab} = 0$; see also ref 44) has been used as a method to obtain the unitary transformation which allows one to obtain the Hamiltonian in the diabatic basis, and then H_{ab}. The procedure, which in principle can be generalized to an arbitrary number of states, opens the way to the inclusion of correlation effects. However, within this approach it becomes crucial to have the ability to perform reliable *ab initio* calculations on systems that may exhibit strong correlation effects, while we will show in this paper that a simple model, which contains the essential physics of the problem, can account for the optical properties related to the et process in a whole class of compounds.

To show in detail the reasons that have drawn us to assess that optical properties of class II and class III MV compounds, such as position and relative intensities of absorption lines in the near-IR−vis, can be understood within a purely electronic picture, in the following section we will start with a simple and didactic example, that of a Ru−L dimer. This is indeed the very first "brick" by which a suitable electronic model for the whole class of bridged Ru compounds can be built and is valid also for partially localized systems. Furthermore, from that example, we have the first indication of the real role of vibronic interaction in these compounds.

(1) Metal−Ligand Units (Dimers). Let us consider for example the system $Ru(NH_3)_5L^{2+}$ studied by Oh, Sano, and Boxer[30] for L = pyz,4,4′-bpy and whose H_{ab} values have been derived by Cave and Newton.[43]

Ru(II) has two electrons in a d_{xz} orbital (taking the ligand ring in the *yz* plane), while a π^* orbital for L is relevant for the back-bonding (metal-to-ligand) interaction.[45] A minimal electronic model can thus be built with two orbitals and two electrons, i.e. with a three-state system if one considers only $S_z = 0$ states. The basic ingredients to be considered are three: the energy gap between the two orbitals ($\Delta = E_L - E_M$), the Coulomb repulsion on the metallic atom (U), and the delocalization, or hopping, term (t). One has then, in second quantization form, the Hamiltonian (M = Ru d_{xz} and L = ligand π^*), which is a version of the well-known Hubbard Hamiltonian:[46]

$$H = \Delta(n_{L\uparrow} + n_{L\downarrow}) + t\sum_{\sigma}(a^{+}_{M,\sigma}a_{L,\sigma} + \text{h.c.}) + Un_{M\uparrow}n_{M\downarrow} \qquad (1)$$

where $a^{+}_{M\sigma}$ ($a_{M\sigma}$) is the creation (annihilation) operator for one electron in the orbital of the metal with spin σ (the index L indicates the same operators for the ligand), $n_{J\sigma} = a^{+}_{J\sigma}a_{J\sigma}$ (J = M, L) is the number operator for the electrons at site J with spin σ.

The basis states with $S_z = 0$, in the notation $|\mathrm{M, L}\rangle$, are

$$|1\rangle = |\uparrow\downarrow,0\rangle,\ |2 = \frac{1}{\sqrt{2}}\Big[|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle\Big],\ |3\rangle = |0,\uparrow\downarrow\rangle \qquad (2)$$

The Hamiltonian matrix for the $Ru(NH_3)_5L^{2+}$ system is then

$$H = \begin{pmatrix} U & t\sqrt{2} & 0 \\ t\sqrt{2} & \Delta & t\sqrt{2} \\ 0 & t\sqrt{2} & 2\Delta \end{pmatrix} \qquad (3)$$

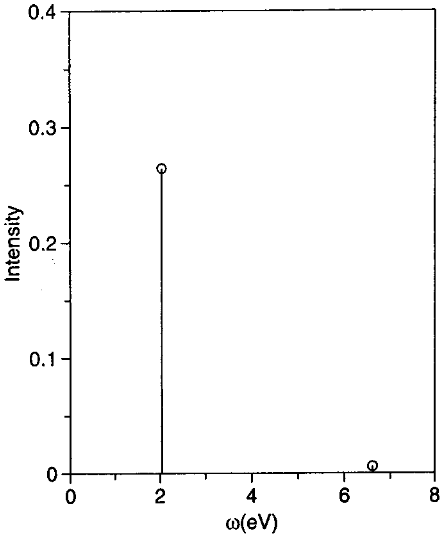

Figure 1. Absorption spectra of the M−L dimer $Ru(NH_3)_5L^{2+}$ (L = pyz, 4,4′-bpy) as computed by the electronic midel Hamiltonian of eq 1 with the parameters given in eq 4. The intensity is in units of the M−L distance *b*.

Eigenvalues and eigenvectors can then be found analytically and have a rather complex form, which we do not report here. However, if one takes "reasonable" values[24] for the three parameters (in eV), such as

$$t = -0.73;\ U = 4.62,\ \text{and}\ \Delta = 5.06 \qquad (4)$$

the following eigenstates are obtained (energies in eV):

$$|g\rangle = 0.747\,908|1\rangle + 0.655\,344|2\rangle + 0.105\,637|3\rangle;\quad E_g = 3.715\,39$$

$$|e_1\rangle = 0.662\ \ 828|1\rangle - 0.728\,670|2\rangle - 0.172\,336|3\rangle;\quad E_{e1} = 5.754\,93$$

$$|e_2\rangle = 0.035\ \ 965|1\rangle - 0.198\,911|2\rangle + 0.979\,357|3\rangle;\quad E_{e2} = 10.329\,7 \qquad (5)$$

The meaning of "reasonable" will be more clear later in the paper. We can anticipate here that the values of the parameters considered are exactly those that allow us to reproduce position and intensity of the bands observed experimentally for the species (see next section) $[(NH_3)_5Ru\text{-pyz-}Ru(NH_3)_5]^{m+}$ (m = 4,5, 6).

The dipole operator for these M−L systems, in second quantization form and taking the origin centered on the ligand orbital, can be written as

$$\mu = -b(n_{M\uparrow} + n_{M\downarrow}) \qquad (6)$$

where b is the Ru−L distance; note that the spectra are not affected by the choice of the origin.

With the dipole of eq 6 and the eigenfunctions of eq 5, we can then easily calculate the spectrum which is shown in Figure 1. The absorption at about 2 eV is the predicted metal-to-ligand charge transfer (MLCT) transition.

Experimentally, for the four cases of L = pyz, 4,4′-bpy, $pyzH^+$, and 4,4′-bpyH^+ (Figures 2 and 3 and Table 2 of ref 30), this transition is found in the range 16 000−20 000 cm^{-1} (∼1.98−2.48 eV). Therefore, the model with the parameters of eq 4, optimized for the Creutz−Taube ion and its homovalent analogues, predicts with a good approximation the position of

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the MLCT transition for the four compounds. In fact, as far as the M → L backbonding interaction is concerned, the π^* orbital of pyz is not expected to be very different from that on one of the two rings of 4,4′-bpy, and thus the values of the parameters, which in principle should be considered in the model when applied to each of the four ligands, are not expected to change very much, except for slight differences in the band gap Δ.

The same model Hamiltonian of eq 1 can be considered for the +3 ions. In that case, since Ru(III) has only one electron in the d_{xz} orbital, one has only two states:

$$|1\rangle = |\uparrow,0\rangle,\ |2\rangle = |0,\uparrow\rangle \tag{7}$$

and the Hamiltonian matrix for the $Ru(NH_3)_5L^{3+}$ is simply

$$H = \begin{pmatrix} 0 & t \\ t & \Delta \end{pmatrix} \tag{8}$$

With the parameters of eq 4, one then obtains the following eigenstates:

$$|g\rangle = -0.981\,296|1\rangle - 0.192\,506|2\rangle;\ E_g = -0.202\,526$$

$$|e\rangle = 0.192\,506|1\rangle - 0.981\,296|2\rangle;\ E_{e1} = 5.262\,53 \tag{9}$$

so that the spectrum will not show any band below 3 eV, as expected from experiments.[47]

Notice that because the model considers only one orbital per site, it is unable to predict correctly the absorption above 3 eV, where transitions involving the inner Ru orbital occur.[22,45]

The two examples above, despite their simplicity, give us two interesting insights. First of all, the Hamiltonian of eq 1 appears to contain the essential ingredients to model Ru−L complexes at various oxidation states (+2 and +3) of ruthenium, which is missing in the two-state models by Hush and PKS where the explicit role of the ligand orbital and correlation effects are both neglected. This finds further confirmation in the study of bridged systems that follows. Second, the intense MLCT transition in the range 16 000−20 000 cm^{-1} for the four M−L dimers, predicted by the model proposed, is the result of a strong electronic delocalization between metal and ligand orbital (see eq 5), as also confirmed by the strong absorption itself. In fact, in case of well-localized states one would expect almost no MLCT transition, since the transition dipole is zero between localized states.[43,44]

The evidence of such a strong M−L delocalization, from both experiments and theoretical electronic models, suggests that vibronic interaction should not be responsible for any substantial shift in the position and relative intensity of the bands. Thus, when all considerations given above are extended to bridged systems, one can expect that also in that case, the position and relative intensities of the bands in the near-IR−vis can be predicted by a purely electronic model. While this can be quite obvious for delocalized (class III) systems, it is not so in case of partially localized (class II) systems where vibronic interaction has always been invoked.

This, of course, does not mean that one can always neglect the effect of nuclear motion. Indeed, it is very relevant in determining the line shape profile and cannot be disregarded when studying properties such as the Stark effect.[29] Furthermore, there can be systems in which electronic delocalization is of the same order of magnitude as the vibronic interaction, and in these cases a purely electronic model would fail; however, it should be noticed that, according to our previous discussion, in this latter case one should expect an absorption with very low intensity in the whole near-IR−vis range.

(2) Bridged Systems. The extension of the concepts discussed in the previous section and, consequently, of the Hubbard Hamiltonian of eq 1 to bridged systems is straightforward. However, we now pay particular attention to the bridging ligand. In fact, there are important differences in the absorption spectra of bridged systems when going from pyz to 4,4′-bpy which require more an adjustment of the model than a simple change in the values of the parameters. Indeed, for the 4,4′-bpy case we have to consider that the two rings are not coplanar and do not give rise to a well delocalized π^* orbital as for pyz. Therefore two connected, but separate, π^* orbitals are needed. Thus, this bridged partially localized (class II) system should be seen as an M−L−L−M rather than an M−L−M system.

(A) M−(L−M)$_n$ Compounds. For bridging ligands that have a π^* orbital well delocalized over the whole molecule, such as pyrazine, the picture in which only one orbital per site holds and one can write the Hubbard Hamiltonian in the general form[26,27]

$$H = \sum_{j,\sigma}^{N_{site}} \epsilon_j n_{j,\sigma} + t \sum_{j,\sigma}^{N_{site}-1} (a^{+}_{j,\sigma} a_{j+1,\sigma} + \text{h.c.}) + U \sum_{m}^{\text{M}-\text{atom}} n_{j,\uparrow} n_{j,\downarrow} \tag{10}$$

where $\epsilon_j = \epsilon_L, \epsilon_M$ ($\Delta = \epsilon_L - \epsilon_M$) is the site energy, and N_{site} is the number of sites ($N_{site} = N_M + N_L$).

The general form of the dipole operator for a M−(L−M)$_n$ system is

$$\mu = \sum_{j,\sigma}^{N_{site}} n_{j,\sigma} \left(j - \frac{N_{site} + 1}{2} \right) \tag{11}$$

where the M−L distance has been taken to be unity for simplicity. We utilize a complete basis set of minimal S_z, that is all $N = \binom{N_{site}}{N_{el\uparrow}} \binom{N_{site}}{N_{el\downarrow}}$ ($N_{el\uparrow}/N_{el\downarrow}$ = total number of electrons with spin up/down) possible configurations and the total number of electrons is given by the simple rule $N_T = N_{Ru(III)} + 2N_{Ru(II)}$.

With the Hamiltonian of eq 10 and the dipole operator of eq 11 we can then calculate the absorption spectra for bridged systems.

In the case of the species $[(NH_3)_5Ru\text{-pyz-}Ru(NH_3)_5]^{m+}$ (m = 4, 5, and 6) this has already been done for a set of parameters different from that of eq 4.[24] We found a very good agreement between calculated and observed spectra as far as the effect of changing the total charge is concerned. In short, we found a peak in the near-IR for only the +5 species and a peak in the visible region only for both +5 and +4 species. However, the positions of the computed peaks and their relative intensity was not precisely those found in the experiments. We then performed a parametric fit of the observed bands, which included the information that the +6 species do not show any absorption in the near-IR−vis. The results obtained are the parameters of eq 4, and the corresponding spectra for the three species are shown in Figure 2.

The agreement with the experimental intensities is notably ameliorated. The near-IR peak for the +5 ion is at 0.607 eV, and that in the visible region is at 2.07 eV, while for the +4 species it is at 1.78 eV, and the relative intensity of the three peaks is in agreement with the experimental findings (see ref 18 and Figures 4 and 5 of ref 30). However, with this new set of parameters the assignment of the peaks remains essentially

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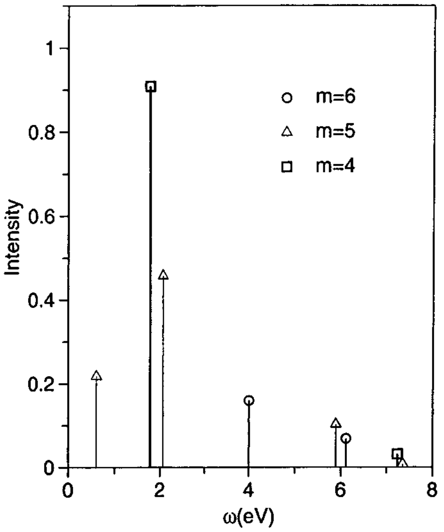

Figure 2. Absorption spectra of the bridged compounds $[(NH_3)_5$Ru-pyz-Ru$(NH_3)_5]^{m+}$ at various total charge (m = 4, 5, 6) as computed by the electronic model Hamiltonian of eq 10 with the same parameters as in Figure 1 (eq 4).

the same as that reported in ref 24 and is in agreement with ref 23, which can be summarized as follows:

(i) the peak in the near-IR for the +5 species, known as intervalence (IT) transition, can be interpreted as having slight ligand-to-metal charge transfer (LMCT) character;

(ii) the peak in the vis for both the +5 and +4 species is essentially a metal-to-ligand charge transfer (MLCT) from a doubly occupied metal orbital.

According to ref 23 both transitions contain IT character, which in this delocalized case means reduction in the bond order.

When the model is applied to longer chain analogues, that is, to the bridged systems synthesized and studied by Von Kameke, Tom, and Taube,[25] again we obtain a good agreement between theoretical prediction and experiment.[26,27] The optical absorption spectra observed in the visible region as a function of the total charge of the ion are very well reproduced with the model Hamiltonian discussed here. Unfortunately there is no measurement available in the near-IR, so the behavior of the calculated peaks in that region cannot be verified with the experimental results. To summarize, we predict that there is a peak in the near-IR only when one or more Ru(II) is present whose frequency decreases upon increasing the length of the chain, that is the number of Ru−pyz units. This behavior is reminiscent of that observed in high-T_c superconductors[48] and is an indication that the system can be a conductor, in accord with some experimental findings.[28] The near-IR peak can be interpreted as a slight LMCT for short chains (see above) but it turns to a sort of MMCT transition (e.g. a transition in which the two states involved have almost the same average charge on the metals but with a different distribution) as the length of the chain increases.

(B) M−L−L−M Compounds. A different situation occurs when the ligand bridging the two metals does not have a π^* orbital well delocalized on the whole molecule, such as for 4,4′-bpy.

The mixed-valent compound $[(NH_3)_5$Ru-4,4′-bpy-Ru$(NH_3)_5]^{5+}$ is considered, unlike $[(NH_3)_5$Ru-pyz-Ru$(NH_3)_5]^{5+}$, to be an example of a localized (class II) compound. Indeed, its absorption spectrum shows a very small band in the near-IR,[30] but a strong absorption in the visible region persists (Figure 6 of ref 30), and the same band is also observed for the +4 ion (Figure 4 in ref 30).

The presence of the band in the visible region, according to the above discussion on the $[Ru(NH_3)_5-L]^{m+}$ (m = 2, 3, and L = pyz, 4,4′-bpy) compounds, suggests that the metal-to-ligand interaction is expected to be very strong. Therefore, one is faced with the question of understanding why the mixed-valent species, in the case of L = 4,4′-bpy, has a near-IR absorption at higher frequency and with intensity reduced by a factor of 5 in comparison with L = pyz (compare Figures 5 and 6 of ref 30). In fact, within a picture that considers only one π^* orbital in analogy to that utilized above for the delocalized systems $[(NH_3)_5$Ru-pyz-Ru$(NH_3)_5]^{m+}$, the model would also predict a strong absorption in the near-IR.

One could then invoke vibronic interaction: in the case of 4,4′-bpy one has a more symmetric line shape than for pyz, and, according to the PKS scheme,[31] the Franck−Condon factors would suggest that the system is partially localized. However, the value for the coupling between electronic and nuclear motion needed to predict such a variation of line shape, in the presence of a strong M−L delocalization as required to explain the MLCT at about 2 eV in both cases of pyz and 4,4′-bpy dimers, should be unrealistically high in comparison to the hopping t and would shift too much both peaks (IT and MLCT). Thus, while the reasons for the more symmetric line shape in the 4,4′-bpy case can be different from that of the Franck−Condon progression in localized two-state systems and should be investigated, one may answer the question within a purely electronic framework.

Indeed, the problem can be solved if one considers the differences between pyz and 4,4′-bpy. The latter ligand is made by two out-of-plane rings connected by a single bond, so that there cannot be a delocalized orbital on the whole molecule, which would require coplanar rings. Therefore, instead of the single π^* orbital considered for pyz, the ligand could now be represented by means of two separate π^* orbitals between which electronic delocalization is very small. Thus, one models the $[(NH_3)_5$Ru-(4,4′-bpy)-Ru$(NH_3)_5]^{m+}$ ions as a $[M-L-L-M]^{m+}$ system in which the M−L hopping integral (t) is the same as that for pyrazine and the L−L hopping (t') is much smaller.

The term t' can be somehow seen as an effective hopping resulting from the coupling of electronic delocalization with the torsion of the two rings of 4,4′-bpy. From this perspective, it would probably be more appropriate to consider for the ligand a coordinate-dependent hopping,[31,32,49] and there is the possibility that this would also explain the symmetric line shape. However, while this approach will be investigated in the future, we will show that in order to discuss the position and intensity of the bands observed in the near-IR−vis, the use of an effective t' in an electronic approach is sufficient.

The model Hamiltonian for the $[M-L-L-M]^{m+}$ system, which is derived from that of eq 10 including the L−L hopping t', can be written as

$$H = \sum_j^{N_{\rm site}} \epsilon_j n_j + t(a_1^+ a_2 + a_3^+ a_4 + \text{h.c.}) + t'(a_2^+ a_3 + \text{h.c.}) + U \sum_j^{\text{M}-\text{atom}} n_{j,\uparrow} n_{j,\downarrow} + U_{\rm L} \sum_j^{\text{L}-\text{site}} n_{j,\uparrow} n_{j,\downarrow} \qquad (12)$$

where we have dropped the spin index for simplicity and added the repulsion term $U_{\rm L}$ on the ligand orbitals for the reason which

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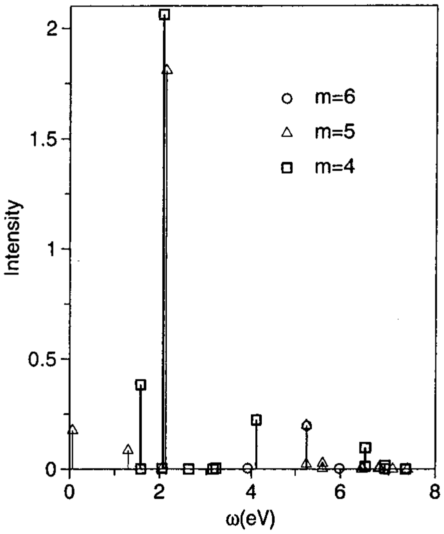

Figure 3. Absorption spectra of the bridged compounds $[(NH_3)_5Ru\text{-}4,4'\text{-bpy-}Ru(NH_3)_5]^{m+}$ at various total charge ($m = 4, 5, 6$) as computed by the electronic model Hamiltonian of eq 12. The three parameters t, Δ, and U are the same as those of Figures 1 and 2 (eq 4), $t' = -0.15$ eV and $U_L = 0$.

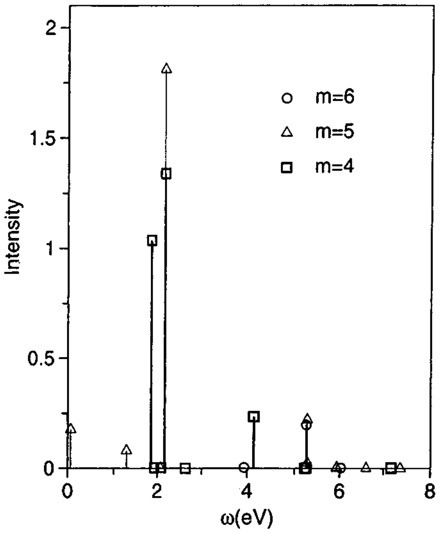

Figure 4. Absorption spectra of the bridged compounds $[(NH_3)_5Ru\text{-}4,4'\text{-bpy-}Ru(NH_3)_5]^{m+}$ at various total charge ($m = 4, 5, 6$) as computed by the electronic model Hamiltonian of eq 12. The three parameters t, Δ, and U are the same as those of Figures 1 and 2 (eq 4), $t' = -0.15$ eV and $U_L = 2.5$ eV.

will be explained below; sites 1 and 4 correspond to the two edge metals, and sites 2 and 3 correspond to the two ligand orbitals.

The dipole operator now has the form

$$\mu = -\left(a + \frac{b}{2}\right)n_1 - \frac{b}{2}n_2 + \frac{b}{2}n_3 + \left(a + \frac{b}{2}\right)n_4 \qquad (13)$$

where a and b are respectively the M−L and L−L distances.

For the three species for $m = 4$, 5, and 6, we have respectively 36, 24, and 16 basis states. We have estimated for a and b the values $a = 3.4$ Å and $b = 2$ Å, as the R−N distance plus half the N−C distance in one ring of 4,4′-bpy and the latter plus half the C−C distance between the two rings, respectively. According to the results discussed above for Ru−L systems, we have considered for t, Δ, and U the values of eq 4 and we have chosen for t' the value $t' = -0.15$ eV $\approx t/5$, according to the intensity ratio of the near-IR band for 4,4′-bpy and pyz +5 MV compounds.

The spectra for the three ions, taking $U_L = 0$ and $U_L = 2.5$ eV, are shown respectively in Figures 3 and 4. It can be seen that, in the near-IR−vis region, as far as position and intensity, the agreement between the calculated spectra and those observed experimentally in Figure 6 of ref 30 is quite good in both cases. The only exception is that in the case of Figure 3, in which $U_L = 0$ as taken for M−(L−M) compounds, the computed spectrum exhibits for the +4 ion a peak at about 1.6 eV ($\approx$13 000 cm^{-1}) which is not observed experimentally. This does not happen for the corresponding spectrum computed for $U_L = 2.5$ eV (Figure 4): in this case the computed spectrum for the +4 ion exhibits two bands around 2 eV which, together, form the observed band centered at about 16 000 cm^{-1} which itself, according to the discussion reported in ref 30, is predicted to be originated by two peaks close to each other. Therefore, the best set of parameters to fit the experimental spectra in the near-IR−vis should be that of Figure 4. Note that the inclusion of U_L is not just for ameliorating the fit but there are reasons, that will be discussed below, that explain why U_L can be disregarded for M−L−M and not for M−L−L−M systems.

Furthermore, the calculations predict a peak at very low frequency (about 0.06 eV, $\approx$500 cm^{-1}) in a region not covered by the experiment and whose intensity is about twice that of the peak at 1.3 eV.

An analysis of the states involved in the various transitions in the near-IR−vis is able to give a precise understanding of the origins of the peaks, as well as of the role played by the Coulomb repulsion on the ligand U_L, neglected in the study of fully delocalized compounds (i.e. those schematized as M−L−M). The results are reported in Table 1, where W_M is the weight (normalized to 1) of configuration with 1, 2, etc. electrons on metal orbitals, D_M is the weight of 1 and 2 doubly occupied metal orbitals, and D_L is the corresponding for ligand orbitals, according to eqs 14 and 15:[24,26,27]

$$W_M(k) = \langle\psi|\hat{W}_M(k)|\psi\rangle;\ \hat{W}_M(k) = \delta(\hat{P}_M,k);\ \hat{P}_M = \sum_{i\in M}^{N_{site}} \hat{P}_i \qquad (14)$$

$$D_M(l) = \langle\psi|\hat{D}_M(l)|\psi\rangle;\ \hat{D}_M(l) = \delta(\hat{B}_M,l);\ \hat{B}_M = \sum_{i\in M}^{N_{site}} \hat{n}_{i,\uparrow}\hat{n}_{i,\downarrow} \qquad (15)$$

In eq 14, k is the number of electrons in the metal, while in eq 15, which can be rewritten for the ligand L by simply exchanging M with L, l is the number of doubly occupied sites.

The δ's appearing in eqs 14 and 15 are simple Kronecker δ's. Their effect on the state $|\psi\rangle$ is to destroy each component, in the configuration space, whose number of electrons on M (or L) is not the one required.

The analysis confirms that U_L has a relevant effect only for the +4 ion, in which the g → e_1 transition is shifted to a little higher energy for $U_L = 2.5$ eV since the weight of doubly occupied ligand orbitals in e_1 is seen to decrease sensibly (compare, for the +4 ion, D_L for e_1 in Table 1). Thus, when $U_L \neq 0$,this transition is essentially of the same nature of that at 2.17 eV (g → e_2), e.g. a MLCT from a doubly occupied metal orbital to a singly occupied ligand orbital (in the lower part of Table 1, $W_M(4)$ and $D_M(1)$ go from 0.33 to 0 and D_L is always very small), while for $U_L = 0$ it appears to be an MLCT with a contribution from doubly occupied metal orbital to doubly occupied ligand orbital. Notice, however, that this does not happen in the case of the three-site model for M−L−M

Table 1. Analysis of the Ground (g) and Excited States (e_1, ..., e_n) Involved in the Near-IR−Vis Transitions for the $[(NH_3)_5Ru\text{-}(4,4'\text{-bpy})\text{-}Ru(NH_3)_5]^{m+}$ ($m = 4$, 5) As Modeled by the Hamiltonian of Eq 12

				W_M				D_M		D_L	
m	state	ω (eV)	total % on M	1	2	3	4	1	2	1	2
				$U_L = 0$							
5	g	0.000	83.5	0.02	0.45	0.53		0.54		0.01	
	e_1	0.067	84.7	0.02	0.42	0.56		0.57		0.01	
	e_2	1.304	66.7	0.02	0.96	0.02		0.02		0.00	
	e_3	2.134	78.7	0.04	0.56	0.40		0.41		0.03	
4	g	0.000	77.2	0.01	0.20	0.48	0.31	0.49	0.31	0.02	0.00
	e_1	1.581	66.5	0.00	0.33	0.67	0.00	0.68	0.00	0.32	0.00
	e_2	2.074	72.8	0.00	0.08	0.92	0.00	0.95	0.00	0.08	0.00
				$U_L = 2.5$ eV							
5	g	0.000	84.1	0.01	0.45	0.54		0.55		0.01	
	e_1	0.064	85.3	0.01	0.41	0.58		0.58		0.00	
	e_2	1.283	66.5	0.02	0.97	0.01		0.02		0.00	
	e_3	2.163	78.9	0.02	0.59	0.39		0.40		0.01	
4	g	0.000	78.3	0.01	0.18	0.48	0.33	0.49	0.33	0.01	0.00
	e_1	1.847	73.7	0.00	0.05	0.95	0.00	0.96	0.00	0.04	0.00
	e_2	2.170	74.1	0.00	0.04	0.96	0.00	0.98		0.03	0.00

compounds, where the ground state has a slightly higher metallic character. Thus, while a Coulomb repulsion term on the ligand π^* orbital(s) is to be expected, its role is not so relevant in M−L−M systems, and indeed its inclusion in the model Hamiltonian of eq 10 only causes a shift of a few wavenumbers in the MLCT peak for the +4 ion.

For the +5 ion, the two relevant transitions (g → e_2 and g → e_3) found, in both cases of $U_L = 0$ and $U_L = 2.5$, at ∼1.3 and ∼2 eV, respectively, have about the same origin of those at ∼2 eV for the +4 ion and discussed above, i.e., a MLCT transition from doubly occupied metals (see Table 1). The only difference, which can be seen from Table 1, is that in the latter (g → e_3) the amount of doubly occupied metal orbitals involved is lower (for $U_L = 2.5$, D_M is 0.55 for *g*, 0.02 for e_2, and 0.40 for e_3).

This is a very important point. Experimentally there is a peak at 1 eV (Figure 6 of ref 30), assigned as an IT transition as is the 0.7 eV peak of the Creutz−Taube ion. Our model predicts a peak at ∼1.3 eV with the same intensity ratio as the ∼2 eV peak as that observed experimentally, and a better fit in the position can be probably found with a more accurate choice of the parameters (taken here as equal to that for the pyz compounds). However, the nature of such a peak predicted by the model is not that of an IT transition, but instead is an MLCT like the peak at ∼2 eV. The model indeed predicts an IT transition at ∼0.06 eV (see Figures 3 and 4 and Table 1), a region not covered by the experiment.

This result, although in contrast with the previous assignments, is very reasonable. First of all, an IT transition at a frequency so high as 1 eV should indicate very strong electron delocalization and thus have a huge intensity, unless a strong vibronic interaction is invoked, but we can exclude that by previous arguments and from the fact that its effect should also be seen in the MLCT transition, which instead is in the 2 eV region as for the pyz compound (where an adiabatic approach is reasonable[24]). Furthermore, if the 1 eV transition was really an IT transition, its behavior under crown ether encapsulation would be the same as that for the Creutz−Taube ion,[21] that is, a slight blue shift upon symmetric encapsulation, and this is not observed. In fact, Hupp and co-workers[50] clearly show that this peak, upon symmetric encapsulation, appears at a slightly lower frequency and thus shows the same behavior as the MLCT. This point will be further discussed in a future paper.[51]

The model above could be easily extended to longer chain Ru−4,4′-bpy compounds ($M-(L-L-M)_n$) as has been done for Ru−pyz systems. However, since to our knowledge these compounds have not been synthesized or studied, we do not report any example here.

Conclusions

In the present article, we have presented and extensively discussed, for the specific case of Ru, an electronic model for bridged transition metal chains which appear to contain all the essential ingredients to reproduce and explain the optical properties in the near-IR−vis.

Our approach somehow distinguishes between delocalized and partially localized compounds, in the sense that the two cases are seen respectively as $M-(L-M)_n$ and $M-(L-L-M)_n$ and the main difference is thus in the presence of a small ligand−ligand interaction causing partial electronic localization.

Basically, the model includes the explicit role of ligand orbitals and contains the effect of electronic correlation (Coulomb repulsion), neglected in most popular two-state approaches.

While it is possible to get a better optimization of the parameters ruling the various effects for each specific case, it is shown that with the same set of parameters the model is consistent in accounting for the observed optical properties of bridged compounds and their parent M−L dimers in both delocalized and partially localized cases, as well as for all possible values for the total charge of the ions, which can be obtained by combining metals of different oxidation states.

The present work focuses on $[(NH_3)_5Ru\text{-}pyz\text{-}Ru(NH_3)_5]^{m+}$, $[(NH_3)_5Ru\text{-}(pyz\text{-}Ru(NH_3)_5)_n]^{m+}$, and $[(NH_3)_5Ru\text{-}(4,4'\text{-bpy})\text{-}Ru(NH_3)_5]^{m+}$ as bridged compounds, but we are convinced that the model proposed can be applied to other bridging ligands and we are also confident that it may be considered for other metals. In this perspective, we will further explore the field in the future.

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