Crown Ether Encapsulation Effects on the Optical Properties of Delocalized and Partially Localized Bridged Ruthenium Dimers

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The effects of crown ether encapsulation on the position of the near-IR−vis bands of $[(NH_3)_5Ru\text{-pyz-}Ru(NH_3)_5]^{m+}$ and $[(NH_3)_5Ru\text{-}(4,4'\text{-bpy})\text{-}Ru(NH_3)_5]^{m+}$ ($m = 4, 5$) have been investigated within a purely electronic picture. The model accounts for the observed behavior and furnishes a theoretical explanation. The near-IR band, observed experimentally around 1 eV, is found to be a metal-to-ligand charge-transfer transition, in contrast to the common idea that ascribes it to an intervalence transition (Ferretti, A.; Lami, A.; Villani, G. *Inorg. Chem.* **1998**, *37*, 2799). The results obtained are a further confirmation that the model proposed contains all the essential ingredients for a basic minimal description of electron transfer in donor−bridge−acceptor systems.

Introduction

Mixed-valence compounds (MV) made by metal atoms bridged by organic ligands are a very interesting and promising class of chemical substances, especially in view of their use in molecular electronics and photonics. Indeed, the presence of metals in different oxidation states with suitable bridging ligands allows that some electrons can move from one metal to the next. This translates in highly polarizable systems which behaves as semiconductors[1] and may exhibit relevant nonlinear optical (NLO) properties.[2,3] Therefore, these compounds can offer a valid alternative to the most popular and studied conjugated polymers, such as polyacetylene- and polythiophene-based compounds.

In this perspective, of particular interest are the chain compounds which one may build bridging Ru atoms, in different oxidation states, with pyrazine (pyz)[1,4] or other organic ligands (see for example refs 5 and 6). Indeed, model calculations indicate that these systems show the typical optical behavior of conductors (the Drude precursor in the optical conductivity spectra[7]), as well as a very intense third harmonic generation.[3]

The first member of the series, made by two pyz-bridged (pyz = pyrazine) $Ru(NH_3)_5$ moieties and having total charge +5 (one Ru(II) and one Ru(III)), is most well-known as Creutz−Taube (CT) ion, being first synthesized and studied by the two authors.[8] For that compound and for its longer chain analogues, we have previously proposed a simple electronic model,[7,9] which accounts for the observed spectral behavior in the near-IR−vis as the total charge varies upon oxidation/reduction. The model has been enriched considering the effect of vibronic interaction, so that the line shape[10] and electrochromic effects[11] can be studied and very good predictions of the experimental results[12] are thus obtained.

Beside the CT ion, well-known to be an example of delocalized system, one should consider partially localized compounds to shed some light on the mechanism of electron delocalization as well as to attain a unified picture for the study of bridged metal lattices. In this case, a prototype system to be considered is still made by two $Ru(NH_3)_5$ moieties, as the CT ion, but the bridging ligand is 4,4′-bpy (bpy = bipyridine) instead of pyz. For this system we have very recently proposed an electronic model,[9] obtained by extending that considered for pyz-bridged compound, which accounts for the observed band positions and their relative intensity in the near-IR−vis at various total charge (i.e. for all the possible combinations of Ru(II) and Ru(III)).[12] Such model assigns the band observed at ∼1 eV to a metal-to-ligand charge transfer transition, differently from the commonly accepted interpretation of being a metal-to-metal (or intervalence) transition.

Here, in the framework of the proposed model for localized and partially localized compounds, we want to study solvatochromic effects, as those experimentally investigated by Hupp and co-workers by crown ether encapsulation of Ru-pyz-Ru ions[13,14] and Ru-(4,4′-bpy)-Ru ions[15,16] (dropping ammonia for simplicity). The aim is to further demonstrate the validity of a purely electronic picture in the understanding of near-IR−vis

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optical properties of mixed-valent Ru compounds, which allows us to be confident that the models proposed can be extended to other mixed-valent systems as well as utilized in a predictive manner.

The Model

The purely electronic model that we have proposed and discussed[7,9] is based on the primary role that d → π^* back-bonding interaction has in the origin of the observed optical properties in the near-IR−vis for MV compounds. From this point of view, the configuration space is reduced in order to consider only one orbital per site. In the specific cases of Ru-pyz-Ru ions and Ru-(4,4′-bpy)-Ru ions, we have a three-site system for the first and a four-site system for the second, respectively. This difference, as explained in detail in ref 9, is due to the very relevant difference between the two ligands and is also responsible for partial localization in the 4,4′-bpy compounds. Indeed, while the role of pyz molecule (an aromatic ring), acting as a bridging ligand between two Ru ions, can be modeled by a single π^* orbital, in the case of 4,4′-bpy (two aromatic rings connected by a single bond) a more appropriate view is that of considering two separate, weakly interacting π^* orbitals. Therefore, while Ru-pyz-Ru ions can be schematized as M−L−M^{m+}, Ru-(4,4′-bpy)-Ru ions will be M−L−L−M^{m+} (for $m = 4, 5, 6$).

For Ru atoms the d_{xz} orbital is considered (taking the ligand ring in the *yz* plane). The three or four orbitals are then filled with a total number of electrons $n = 2N_{\mathrm{Ru(II)}} + N_{\mathrm{Ru(III)}}$ ($N_{\mathrm{Ru(II)}}$ = number of Ru(II) in the molecule) and all configuration with minimal S_z are included in the configuration space, whose dimension is then $\binom{N_{\mathrm{site}}}{n_\uparrow}\binom{N_{\mathrm{site}}}{n_\downarrow}$ ($n = n_\uparrow + n_\downarrow$).

Basic ingredients of the model are the electronic hopping (or resonance integral) between adjacent sites (t and t' for M−L and L−L hopping, respectively), the energy difference between ligand and metal orbitals ($\Delta = \epsilon_{\mathrm{L}} - \epsilon_{\mathrm{Ru}}$), and the Coulomb repulsion (U and U_{L} for metal and ligand sites, respectively). Thus, one can write the Hubbard Hamiltonian[18] for delocalized M−L−M (H_{d}) and for partially localized M−L−L−M (H_{pl}) compounds:[9]

$$H_{\mathrm{d}} = \sum_{\sigma}[\Delta n_{2,\sigma} + t(a^{+}_{1,\sigma}a_{2,\sigma} + a^{+}_{2,\sigma}a_{3,\sigma} + h.c.)] + U\sum_{j}^{M_{\mathrm{site}}} n_{j,\uparrow}n_{j,\downarrow} \quad (1)$$

$$H_{\mathrm{pl}} = \sum_{\sigma}[\Delta(n_{2,\sigma} + n_{3,\sigma}) + t(a^{+}_{1,\sigma}a_{2,\sigma} + a^{+}_{3,\sigma}a_{4,\sigma} + h.c.) + t'(a^{+}_{2,\sigma}a_{3,\sigma} + h.c.)] + U\sum_{j}^{M_{\mathrm{site}}} n_{j,\uparrow}n_{j,\downarrow} + U_{\mathrm{L}}\sum_{j}^{L_{\mathrm{site}}} n_{j,\uparrow}n_{j,\downarrow} \quad (2)$$

where, as usual, $a^{+}_{j\sigma}$ ($a_{j\sigma}$) is the creation (annihilation) operator for one electron with spin σ in the orbital of site j, $n_{j,\sigma} = \epsilon^{+}_{j,\sigma}\epsilon_{j,\sigma}$. In H_{d} metals are sites 1 and 3 and ligand is site 2, while in H_{pl} metals are sites 1 and 4 and ligands are sites 2 and 3.

For the two cases the dipole operator, respectively μ_{d} and μ_{pl}, has the form

$$\mu_{\mathrm{d}} = \sum_{\sigma}(n_{3,\sigma} - n_{1,\sigma}) \quad (3)$$

$$\mu_{\mathrm{pl}} = \sum_{\sigma}[(a + b)n_{4,\sigma} + bn_{3,\sigma} - bn_{2,\sigma} - (a + b)n_{1,\sigma}] \quad (4)$$

where for M−L−M systems we have taken the M−L distance as unity, while for M−L−L−M systems *a* and *b* are respectively the M−L and L−L distances. We have estimated for *a* and *b* the values $a = 3.4$ Å and $b = 2$ Å, respectively, as the R−N distance plus half the N−C distance in one ring of 4,4′-bpy and this latter plus half the C−C distance between the two rings.

The model Hamiltonians of eqs 1 and 2 with the dipole operators of eqs 3 and 4 have been found to be able to predict and assign the near-IR−vis bands for, respectively, Ru-pyz-Ru^{m+} and Ru-(4,4′-bpy)-Ru^{m+} ions, as the total charge *m* varies from 4 to 6.[9] For H_{d} the best parameters, optimized for the band positions, are $t = -0.73$ eV, $U = 4.62$ eV, $\Delta = 5.06$ eV. In H_{pl} we have taken the same values of t, U, and Δ, since we do not expect that these parameters change significantly going from pyz to 4,4′-bpy, $t' = -0.15 \approx t/5$, and $U_{\mathrm{L}} = 2.5$.[9]

The ground (g) and excited (e_i) states involved in the electronic transitions in the near-IR−vis have been analyzed by means of the quantities discussed in our previous papers[7,9,10] to study the changes observed upon crown encapsulation. However, since here the results of the analysis can be discussed without explicitly invoking such quantities, we report here only P_i, the electron population on site i (normalized to 1), defined by

$$P_i = \langle\psi|\hat{P}_i|\psi\rangle;\ \hat{P}_i = \hat{n}_{i\uparrow} + \hat{n}_{i\downarrow} \quad (5)$$

which gives useful information for asymmetric encapsulation.

Results and Discussion

The success of the electronic model in reproducing and explaining the near-IR−vis bands of pyz- and 4,4′-bpy-bridged Ru ions has stimulated further investigations on its capabilities. As a natural further step we study here solvatochromic effects.

Experimentally, beside all the work that has been done on the effect of various solvents on the optical properties of localized and delocalized compounds, there are very interesting and systematic works concerning the effect of crown ether encapsulation for both Ru-pyz-Ru and Ru-(4,4′-bpy)-Ru compounds,[13−16] which can be compared with our theoretical results.

Crown ethers are known to make hydrogen bonds with ammonia hydrogens and thus, acting as electron donors, cause an increase of electron density on Ru. Therefore, upon crown encapsulation, we can expect Ru d orbitals to be shifted at higher energy, while ligand orbitals are only slightly influenced. This observation, as already discussed in ref 14, suggests that the energy difference between ligand and metal orbitals Δ is expected to decrease slightly. The same effect can be seen introducing an electron donor solvent in electronic calculations on Ru-L dimers.[19,20] The authors of ref 14 estimate this variation within a Hückel three-site model, first proposed by Ondrechen et al.,[17] and find that Δ should decrease by about 700 cm^{-1}, while the delocalization term is found to be almost crown-invariant (a maximum decrease of less than 100 cm^{-1} upon encapsulation).

The increased electron density on Ru upon crown encapsulation is expected to cause the Ru d orbitals to contract. This, which is a minor effect compared with that on Δ, results in a decrease of d−π^* resonance integral *t*. Ab initio calculations on the Ru-pyz system in various solvents[20] indicate that d−π^*

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overlap decreases as the solvent donor number increases, but this is the resulting effect of the decrease of Δ, slightly compensated by the decrease of t which can be argued invoking orbital contraction.[21] Therefore, in the present study we have also taken this effect into account. While we have kept U at the same value of 4.62 eV, when a $Ru(NH_3)_5$ moiety is encapsulated by a crown ether we have taken $t = -0.715$ eV and $\Delta = 4.85$ eV instead of the −0.73 and 5.06 eV for no complexation. These parameter values have been chosen optimizing the band shifts for the symmetrically encapsulated $[Ru\text{-}pyz\text{-}Ru]^{+5}$ ion and utilized in all other cases considered in this work. Their values are different from those found in ref 14 since our model, in comparison with the Hückel three-site model, also contains the Coulomb repulsion term (U term), needed for a full description of the optical properties of bridged compounds as the total charge varies (i.e. changing the oxidation state of the metals).[7,9,10]

For clarity, we separate the discussion into two subsections.

(a) Ru-pyz-Ru Ions. When a crown ether is added, the near-IR band, known as the intervalence (IT) band, present in the +5 ion, is always blue-shifted, but the shift is higher when only one of the two $Ru(NH_3)_5$ moieties is surrounded by a crown ether molecule (asymmetric complexation). In addition, the IT for the asymmetric complex has a more symmetric line shape. In Figure 1 of ref 13, this is shown for a *trans*-pyridine-substituted analogue of the Creutz−Taube ion, and the IT band, which is centered around 0.71 eV (∼1750 nm) without complexation, is observed at ∼0.83 eV (∼1500 nm) upon asymmetric complexation but at ∼0.74 eV (∼1680 nm) for symmetric complexation.

Further experimental study, reported in ref 14, is devoted to the effect of symmetric crown complexation by various ethers, in both the IT and MLCT transitions of the CT ion. The authors found that the blue-shift of the IT transition ranges between 60 and 80 cm^{-1} (∼0.0074−0.01 eV), with the IT band at 5500 cm^{-1} (∼0.68 eV), and that the MLCT transition is red-shifted about 10-fold for all crowns except one.

This behavior is reproduced by the model Hamiltonian of eq 1. In Figure 1 the IT (a) and MLCT (b) bands are shown, and it can be seen that the IT band goes from 0.607 eV without crown to 0.627 eV for asymmetric complexation and is at 0.614 eV for symmetric complexation. The MLCT transition, instead, is monotonically red-shifted and goes from 2.07 eV without crown to 2.04 eV for asymmetric crown and is at 2.00 eV for symmetric complexation. Notice that the parameters t and Δ for the encapsulated Ru site have been changed in order to obtain a good estimate of the observed variation in the position of IT and MLCT bands for the symmetrically encapsulated case. However, the band shift for the asymmetrical case, in agreement with the experiments, is a consequence of this choice but is independent from optimization.

While no comparison can be made concerning the line shape profile, since we do not include nuclear degrees of freedom at this stage, the model is able to give a good description of the variations upon encapsulation as far as the position of the bands is concerned.

The analysis of the states involved in the IT and MLCT transitions,[7,9,10] not reported here with the exception of the distribution of electron population on the sites (Table 1), reveals that the nature of the two transitions[10] is not changed by crown encapsulation. IT transition behaves always as a slight ligand-to-metal transition (LMCT), while the MLCT appears as an electron transfer from a doubly occupied metal orbital to an empty ligand orbital. Upon encapsulation there are, of course, little differences in the weight of various configurations forming the ground and the excited states, which are responsible of the variations observed in the spectra but their connection is not straightforward.

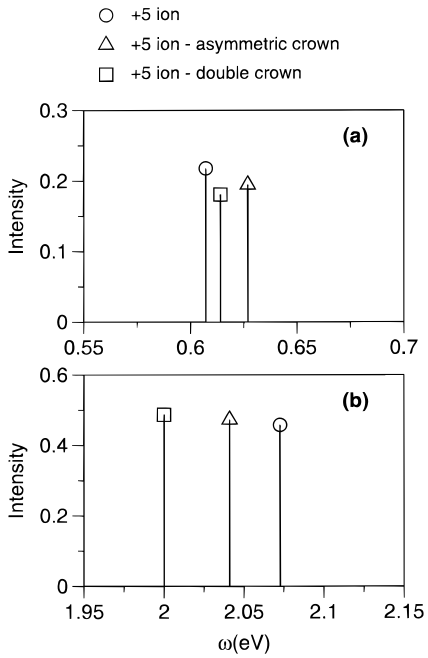

Figure 1. Near-IR−vis computed absorption spectra of the Creutz−Taube ion (+5) upon crown encapsulation (model Hamiltonian of eq 1): (a) near-IR (intervalence; IT) transition; (b) MLCT transition.

Table 1. Distribution of Electron Population (Eq 5) in the Ground (g) and Excited States (e_1,..., e_n) Involved in the Near-IR−Vis Transitions for the $[(NH_3)_5Ru\text{-}pyz\text{-}Ru(NH_3)_5]^{m+}$ (m = 4, 5) with Asymmetric Encapsulation

			total %	P_i		
m	state	ω (eV)	on M	Ru_1	pyz	Ru_2
5	g	0.000	83.5	0.443	0.165	0.392
	e_1	0.627	86.6	0.417	0.134	0.449
	e_2	2.041	78.1	0.398	0.219	0.383
4	g	0.000	82.3	0.418	0.177	0.405
	e_1	1.721	74.3	0.377	0.257	0.366

In case of asymmetric encapsulation, since the symmetry of the Hamiltonian has now been broken, we can obtain some new information from the electronic population of various sites, as computed from eq 5 and reported in Table 1, where Ru_2 is the encapsulated Ru site. The ground state (g) of the +5 ion shows that the encapsulated Ru site is less populated than the other, as expected due to the effect of a slightly smaller Δ for the encapsulated $Ru(NH_3)_5$ moiety which results in a relative stabilization of the other. The opposite is seen for the excited-state e_1: the $g \rightarrow e_1$ transition (IT) thus appears as a real [II−III] → [III,II] transition, even if the transferred charge is much less than 1. However, since the total population of the metals increases, globally the transition results in a slight ligand-to-metal charge transfer. Accordingly, the MLCT transition $g \rightarrow e_2$ appears as a charge transfer mostly from the free Ru (Ru_1 in Table 1) to the ligand.

We also report in Figure 2 the results obtained for the +4 ion, for which no experimental result is available. Upon encapsulation, the MLCT transition, which is the only band

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(21) While performing the calculations of ref 20, the authors noticed that Ru d orbitals, under the action of electron donor solvents, appear to contract. Further investigation is in progress in order to quantify such an effect.

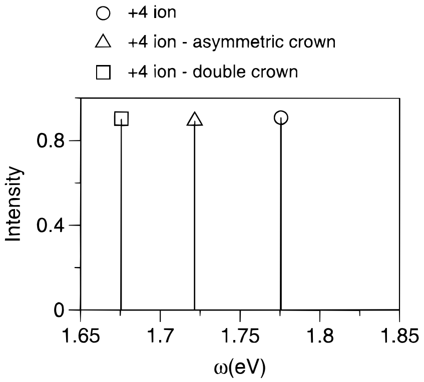

Figure 2. Computed MLCT transition for the [Ru$(NH_3)_5$-pyz-Ru$(NH_3)_5$]$^{+4}$ ion upon crown encapsulation (model Hamiltonian of eq 1).

observed in the near-IR−vis, has the same behavior as the MLCT for the +5 ion, namely, a monotonic red-shift. The transition is a charge transfer that interests mainly configurations with two doubly occupied metals,[10] independently from the encapsulation. For the asymmetric case, the ground state appears less asymmetric than for the +5 ion (see Table 1) and the MLCT is more or less the same for both Ru, differently from the +5 ion, so that the asymmetry is unchanged by the transition. This can be explained considering that the MLCT is from doubly occupied metal orbitals and that these, for the asymmetrically encapsulated +5 ion, are due mainly to the Ru atom with no encapsulation, while for the +4 ion both Ru tend to be doubly occupied.

It is worthwhile to notice that for Ru-pyz-Ru ions, crown complexation has the same effect of changing the solvent from weak to strong electron donors.[22] Therefore, all the considerations done on the role of the crown in affecting the parameters of the model Hamiltonian of eq 1 can be straightforwardly applied to solvent effects.

(b) Ru-(4,4′-bpy)-Ru Ions. [Ru-(4,4′-bpy)-Ru]$^{+5}$ shows a band at ~1 eV, whose intensity is about $^1/_5$ of the IT band for pyz compound, also assigned as an IT, and a band at ~2 eV, the MLCT transition.[12] The model Hamiltonian of eq 2 is able to predict these two transitions but provides a different assignment of the 1 eV band. Indeed, this transition appears to be an MLCT involving a different amount of doubly occupied metal sites than that at 2 eV,[9] while a very low-frequency transition is predicted (~0.06 eV) that is of the same nature of the so-called IT for the pyz-bridged compound.

It should be underlined that the assignment of the ~1 eV transition as an MLCT transition, predicted by our model, is in contrast with the widely accepted view that ascribes the near-IR transition as an IT (or metal−metal charge transfer, MMCT). While details have also been given in ref 9, where the model was first proposed and studied, it is worthwhile to discuss here how the MLCT assignment is not in contrast with some evidence which has been interpreted as a demonstration of IT character of such transition. It is known than when a spacer (ethylene or phenyl) is added between the two rings of 4,4′-bpy, there is a systematic blue-shift and a corresponding decrease of the intensity of the band at ~1 eV, while the opposite is seen for the ~2 eV band.[23] This can be predicted within the picture of our model. Indeed, although the spacer is not expected to greatly alter the energy of the π* orbital centered on each pyridine ring, their resonance integral (t') should be lowered (since their distance increases) and this is seen to cause the observed trend. This can be understood if one remembers that the two MLCT transitions (at ~1 and ~2 eV) interest two different linear combinations of the two ligand π* orbitals, where only one interacts strongly with Ru, thus also explaining the low intensity of the ~1 eV band in comparison to that in the visible. For instance, reducing t' from −0.15 to −0.10 eV, we obtain the following near-IR−vis spectra for the +5 ion (energies in eV):

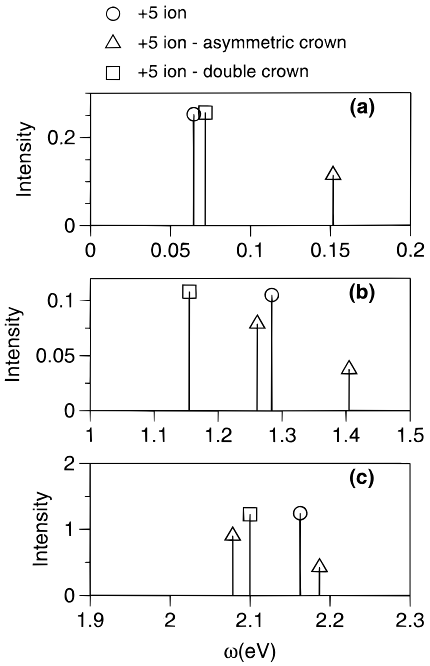

Figure 3. Near-IR−vis computed absorption spectra of the [Ru$(NH_3)_5$-(4,4′-bpy)-Ru$(NH_3)_5$]$^{+5}$ ion upon crown encapsulation (model Hamiltonian of eq 2): (a) low-frequency (intervalence; IT) transition; (b) MLCT transitions at ~1 eV; (c) MLCT transitions at ~2 eV.

t'	ω_1	I_1	ω_2	I_2
−0.15	1.283	0.105	2.163	1.249
−0.10	1.297	0.049	2.128	1.351

where ω_i and I_i (i = 1, 2) are respectively the position and computed intensity for the two MLCT lines.

Experimentally, for the bpy compound, the dependence of the band heads on the crown concentration has been investigated.[15,16] As far as the ~1 eV band is concerned, it is seen that upon adding the crown, its frequency first increases, reaches a maximum associated with the formation of asymmetrically encapsulated ion, and then decreases until a stationary value is reached for a frequency which is slightly smaller than that without any crown ether.[15] Instead, the MLCT transition frequency is seen to decrease monotonically when the crown is added,[15,16] reaching a stationary value that depends on the ether considered (1080−1560 cm^{-1}).[16]

Predictions of the model of eq 2 are reported in Figure 3. The origin of the transitions in the near-IR−vis is basically the same independently from crown encapsulation, but some new features appear in the case of asymmetric encapsulation, which are discussed below.

The IT band, which according to our previous findings is at ~0.06 eV without encapsulation, is shown to behave similarly to the 0.7 eV band of the corresponding pyz-bridged complex. Indeed, asymmetric encapsulation causes a blue-shift of ~700 cm^{-1} which reduces to ~60 for symmetric encapsulation (Figure

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Table 2. Distribution of Electron Population (Eq 5) in 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) with Asymmetric Encapsulation

				P_i			
m	state	*ω* (eV)	total % on M	Ru_1	py_1	py_2	Ru_2
5	g	0.000	84.4	0.509	0.138	0.018	0.335
	e_1	0.152	83.4	0.339	0.014	0.152	0.495
	e_2	1.261	66.6	0.333	0.163	0.171	0.333
	e_3	1.405	66.6	0.333	0.171	0.163	0.333
	e_4	2.078	80.0	0.445	0.162	0.038	0.355
	e_5	2.187	80.5	0.349	0.043	0.152	0.456
4	g	0.000	77.1	0.392	0.109	0.120	0.379
	e_1	1.758	73.7	0.463	0.233	0.030	0.274
	e_2	1.942	74.1	0.300	0.061	0.204	0.435
	e_3	2.039	74.6	0.386	0.127	0.127	0.360
	e_4	2.162	73.1	0.327	0.104	0.164	0.404

3a). An analysis of the transition according to eq 5 (Table 2) reveals that, as for the pyz-bridged complex, the g → e_1 transition is a sort of real [II−III] → [III,II] transition but differently from that (as well as from symmetric and no encapsulation) it has a slight metal-to-ligand character. This should not be surprising because e_1 is the result of the antisymmetric counterpart of the ground state (which is symmetric) perturbed by the finite size effect. Indeed, for pyz-bridged systems e_1 is known to be subject to the same change when going to longer chain analogues of the Creutz−Taube ion.[7] However, there is neither experimental study nor any other evidence of this transition.

The ∼1 eV transition is split into two bands separated by ∼1100 cm^{-1} for asymmetric encapsulation, while restoring the symmetry by double encapsulation the band (single again) appears ∼1050 cm^{-1} below that without any crown (Figure 3b). To compare these results with those observed experimentally, we have to take into account that in the present calculations we have neglected vibrations. In fact, reasonably the two bands predicted for asymmetric encapsulation would merge into one when including the vibrational ladder, and the band maxima should then be at higher frequency than without encapsulation. This appears more reasonable when noticing that the two excited states (e_2 and e_3) involved have the same population on the two metal while that on the two π* of the bpy are exchanged (Table 2). However, while in our next study we will investigate the effect of the inclusion of vibrational degrees of freedom, as already performed for pyz-bridged Ru dimers,[10] we can say that, at least qualitatively, the crown dependence of the ∼1 eV band is reproduced. A quantitative prediction would require a proper choice of the set of parameters of the model Hamiltonian for Ru-(4,4′-bpy)-Ru (which would also depend on the specific crown ether considered), which is beyond the scope of the present work, where we want to show that with the same set of parameters as for Ru-pyz-Ru, besides reproducing the spectra in the near-IR−vis,[9] we can also obtain the qualitative behavior upon crown ether encapsulation.

The splitting upon asymmetric encapsulation also occurs for the MLCT transition in the 2 eV region. The excited states involved (e_4 and e_5) are about mirror images (Table 2) and, according to the considerations above, we could expect that the inclusion of vibrations would take the band head in the middle of that for symmetric encapsulated and no encapsulated complexes, in qualitative agreement with experimental findings.

As far as the corresponding monovalent $[Ru\text{-}(4,4'\text{-bpy})\text{-}Ru]^{+4}$ ion is concerned, there are no experimental results available. However, our predictions are reported in Figure 4. As already pointed out,[9] the observed MLCT band[12] is made by two peaks which, upon crown ether encapsulation, are monotonically blue-shifted. In case of asymmetric encapsulation, there are instead four peaks which cover a slightly wider frequency range. Thus, we can conjecture that in this case the width of the MLCT band should be greater than that for symmetric and no encapsulation.

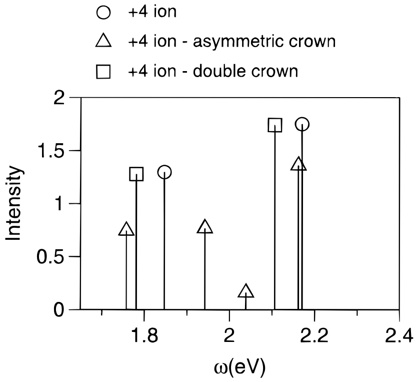

Figure 4. Computed MLCT transitions for the $[Ru(NH_3)_5\text{-}(4,4'\text{-bpy})\text{-}Ru(NH_3)_5]^{+4}$ ion upon crown encapsulation (model Hamiltonian of eq 2).

In this case of Ru-(4,4′-bpy)-Ru ions, the effect of crown encapsulation is not always the same of that of changing solvent from weak to strong electron donors. The peak for the +5 ion, discussed above and found at ∼1 eV in ref 12, is strongly solvent-dependent,[24,25] in contrast to the IT band for the corresponding pyz-bridged ion. Furthermore, this dependence is not monotonic with the strength of electron donation,[25] it is instead monotonic with the reorganization energy.[24] This is somewhat puzzling, especially in light of the consistency found between crown encapsulation and solvent effect in the case of pyz-bridged system, where the two effects appear thus to be ruled by electron donation and the usefulness of Marcus−Hush theory has also been debated.[26]

A possible explanation can be found in the differences between the two ligands. In fact, one can expect 4,4′-bpy to feel the solvent differently from pyz. The latter is quite insensitive to the solvent, and the variations observed in the spectra are due to the metallic d orbitals that, in contrast, strongly feel the solvent change. Instead, in the case of 4,4′-bpy, one can expect that the solvent affects the angle between the two rings, thus changing the L−L delocalization (t'), and this is not an effect that can be related only to electron donation. This does not happen for crown ether encapsulation, where only electronic factors are involved. Notice that t' does not much affect the MLCT transition at ∼2 eV, which is at about the same frequency for pyz and 4,4′-bpy, thus one should expect that solvent effect and crown encapsulation behaves consistently for this transition. This idea is for now just an hypothesis which requires further study, since even a qualitative estimate of these effects of the solvents is not very simple. Furthermore, another possible explanation, not in contrast with the above, can be given within the small polaron picture. Indeed, when the electron transfer (et) process between the two rings is also coupled with solvent degrees of freedom, an increase of the dielectric constant leads to an increase of the effective mass of the electron and, consequently, to a decrease of the effective hopping (and thus to a blue-shift of the ∼1 eV band).

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Conclusions

We have studied, for delocalized and partially localized bridged Ru dimers, solvatochromic effects on the optical spectra in the near-IR−vis, such as those due to crown ether encapsulation. While for the study of the variations of line shape profiles the inclusion of vibrational degrees of freedom is required, a purely electronic picture is sufficient to reproduce and explain the band shifts going from the free molecule to asymmetric and symmetric encapsulation. Thus the results obtained confirm that the proposed model, despite its crudeness and simplicity, is able to capture the essential features underlying the near-IR−vis optical properties of mixed-valent compounds. The apparent inconsistency between crown encapsulation and solvent effects, which characterizes the partially localized [Ru-(4,4′-bpy)-Ru]$^{+5}$ ion, is, however, a signal that further theoretical and experimental investigations are needed.

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