Intervalence Electron Transfer in Pentaammineruthenium Complexes of Dipyridylpolyenes, Dipyridylthiophene, and Dipyridylfuran

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Intervalence transitions have been observed between pentaammineruthenium(II) and -ruthenium(III) groups linked by dipyridylpolyenes, dipyridylthiophene, and dipyridylfuran. For all compounds, the comproportionation constants have been determined, to obtain corrected spectra of the mixed-valence forms, and the intervalence band profiles have been obtained by spectral deconvolution. The longest dipyridylpolyenes (with 3 and 4 double bonds) give only ill-defined bands, which does not allow us to reach definitive conclusions on the decay law of the electronic interaction with distance. On the contrary, dipyridylthiophene and -furan present a better resolution of the intervalence transition, which is ascribed to a better coplanarity and rigidity.

Introduction

The study of electron transfer is a subject of great fundamental importance, particularly in the field of molecular electronics. It is indeed crucial to devise molecules allowing an intramolecular electron transfer between two redox sites linked by a bridge and to establish rules allowing the prediction and mastery of the electron propagation through this bridge. In a previous paper,[1] we have shown that ruthenium complexes linked by α-ω-dipyridylpolyenes exhibit measurable intervalence transitions when the corresponding mixed-valence species are generated by a partial oxidation. This corresopnds in fact to an *extension* (in both senses of the word!) of the seminal work of Taube and collaborators[2] using pyrazine, 4,4′-bipyridine, and dipyridylethylene as bridging ligands.

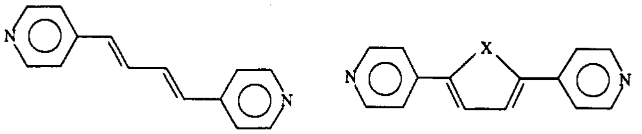
Thus the intervalence method to study intramolecular electron transfer is not new. But it displays some specific advantages over the more sophisticated methods based on flash photolysis. The experiment is simple, and more important, it is essentially insensitive to intermolecular electron transfer. This is due to the very small probability to have the reduced site of one molecule in close proximity of the oxidized one of a different molecule, because, at least in the present systems, they carry charges of the same sign. Thus a large number of experimental results are now available,[3] allowing the rationalization of the influence of the bridge structure on electron transfer.

However, in our previous paper[1] the spectra were recorded in nitrobenzene, a medium in which the determination of the comproportionation constant—and thus the subsequent correction of the spectra—is not trivial. Furthermore, due to the type of spectrophotometer used, the spectra were obtained in two parts (UV–visible, on one hand, and near-IR, on the other hand), which precluded an accurate exploitation of the spectra through mathematical deconvolution. This was noticed by Reimers and Hush[4,5] in more recent papers devoted to the explotitation of intervalence spectra to determine effective through-ligand coupling between metallic sites.

In the following, we describe new results obtained in normal water and D_2O for the compounds $[(NH_3)_5Ru(py){-}(CH{=}CH)_n{-}(py)Ru(NH_3)_5]^{5+}$ (n = 2–4), which will be abbreviated as **Ru–*n*-Ru**. Although the resolution of the intervalence band with respect to the nearby charge-transfer transition is less good than in nitrobenzene, the measurements are more accurate, because the determination of the comproportionation constant is possible, and a number of experimental problems (solvent purity, ion pairing effects) are minimized. We have thus obtained *corrected spectra* and have been able to extract the shape of the intervalence bands through deconvolution, which permits an evaluation of the coupling parameter using the simple procedure described by Hush in 1967.[6,7]

It was also interesting to compare with other conjugated ligands. In a recent paper, some of us[8] have described new conjugation-extended viologens in which the two pyridinium parts of the viologen are linked by an heterocycle such as furan or thiophene. This gives stable systems which exhibit interesting redox properties different from the conjugation-extended viologens having a polyene or phenylene bridge. The precursors of these viologens, i.e. dipyridylfuran and -thiophene have been used here to prepare binuclear ruthenium complexes, which are denoted **Ru–BPF–Ru** and **Ru–BPTh–Ru** in the following.

Thus we have the possibility to compare electron transfer through systems which are in principle equivalent, when the number of formal double bonds is considered:



X = O, S

The experimental comparison between these ligands is performed, and an analysis of the strength of the interaction through extended Huckel calculations is presented.

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(1) Woitellier, S.; Launay, J.-P.; Spangler, C. W. *Inorg. Chem.* **1989**, *28*, 758.

(2) Sutton, J. E.; Sutton, P. M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 1017. Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125.

(3) Creutz, C. *Progr. Inorg. Chem.* **1983**, *30*, 1.

(4) Reimers, J. R.; Hush, N. S. *Inorg. Chem.* **1990**, *29*, 3686.

(5) Reimers, J. R.; Hush, N. S. *Inorg. Chem.* **1990**, *29*, 4510.

(6) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391. The operational formula is given in: Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135.

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Experimental Section

Dipyridylpolyenes were prepared by a procedure already described.[1] Dipyridylfuran and -thiophene were obtained as described in ref 9. Binuclear pentammineruthenium complexes were obtained by interaction of the corresponding ligands with $[(NH_3)_5Ru(H_2O)]\cdot H_2O$[1] in a methanol/acetone mixture, followed by precipitation with diethyl ether.

Elemental analyses are given below for the two new complexes of dipyridylfuran and dipyridylthiophene. Anal. Calcd for $[(NH_3)_5Ru\text{–}BPF\text{–}Ru(NH_3)_5](PF_6)_4\cdot{}^3/_4CH_3COCH_3$: C, 15.84; H, 3.65; N, 13.85; P, 10.21. Found: C, 15.65; H, 3.72; N, 13.68; P, 10.16. The presence of $^3/_4$ molecule of acetone is confirmed by ^1H NMR in D_2O of the ruthenium complex and the integration. Anal. Calcd for $[(NH_3)_5Ru\text{–}BPTh\text{–}Ru(NH_3)_5](PF_6)_4\cdot 0.6PF_6$: C, 13.4; H, 3.21; N, 13.39; S, 2.55; P, 11.35. Found: C, 13.44; H, 3.32; N, 13.69; S, 2.69; P, 11.47. The analysis is consistent with a partial oxidation of the sample, which was confirmed by the UV–visible spectrum (ratio between ligand band and charge-transfer band). This has been taken into account in the oxidation experiments.

Cyclic voltammetry was made using an Electromat 2000 system (ISMP Technologie) with a platinum wire as working electrode and a satured calomel electrode as reference electrode.

Intervalence bands and comproportionation constants relative to the equilibrium

$$[\text{III–III}] + [\text{II–II}] \rightleftarrows 2[\text{II–III}] \qquad (1)$$

(where the Roman numerals refer to the oxidation states of the ruthenium atoms) were determined using an automatic titration system. It was built from an automatic dispensor (Metrohm Dosimate 665) controlled by a homemade automatic time switch, a peristaltic pump with C-flex tubing, and 1-cm flow-cell located in the cavity of a UV-PC 3101 spectrophotometer.

A solution of the starting binuclear ruthenium(II) complex in water or deuterium oxide (30 mL) was prepared and placed in the titration cell. For recording of intervalence transitions, the concentration was generally 2×10^{-4} mol·L^{-1} for the complexes of dipyridylpolyenes (i.e. near saturation) or 1.5×10^{-3} mol·L^{-1} for the more soluble complexes of dipyridylthiophene and dipyridylfuran. Spectral simulation required also the recording of charge-transfer band profiles, which was performed in another titration with concentration 7×10^{-5} mol·L^{-1}. In the case of dipyridylpolyenes complexes, the oxidizing agent was a solution of iodine in either water or deuterium oxide, with concentration 0.015 mol·L^{-1} (plus 0.01 mol·L^{-1} potassium iodide) for recording intervalence transitions or 0.005 mol·L^{-1} (plus 0.033 mol·L^{-1} potassium iodide) for recording charge-transfer bands. For dipyridylthiophene and -furan complexes, the concentrated solutions were titrated by 0.1 mol·L^{-1} iodine containing 0.066 mol·L^{-1} potassium iodide.

For chemical oxidations, the apparatus was set so that after each addition of the oxidizing agent (typically 15 μL), the solution was allowed to mix for 2 min, and then a spectrum was recorded. A series of 10–15 spectra corresponding to progressive oxidation from II–II to III–III was registered. To determine K_c, the following law deduced from equilibrium 1 and mass conservation equations was used:

$$y = \{-K_c + [K_c^2 - K_c x(4 - K_c)(x - 2)]^{1/2}\}(4 - K_c)^{-1}C_{tot.} \qquad (2)$$

where y is the concentration of mixed-valence species, x is the number of oxidizing equivalents per mole of binuclear compound ($0 < x < 2$), and $C_{tot.}$ is the total concentration of the ruthenium complexes, i.e. the sum of the III–III, II–II, and II–III concentrations. The y concentration is proportional to the excess optical density in the near-infrared, where II–III is the main absorbing species. By using the excess optical density (or excess apparent extinction coefficient), i.e. the optical density measured with respect to a base line connecting the initial and final spectra, the procedure takes into account a possible residual absorption of II–II or III–III (see Figure 1). The fitting of experimental results of eq 2 by a least-squares procedure thus provides K_c from which the corrected spectrum of II–III is easily calculated.

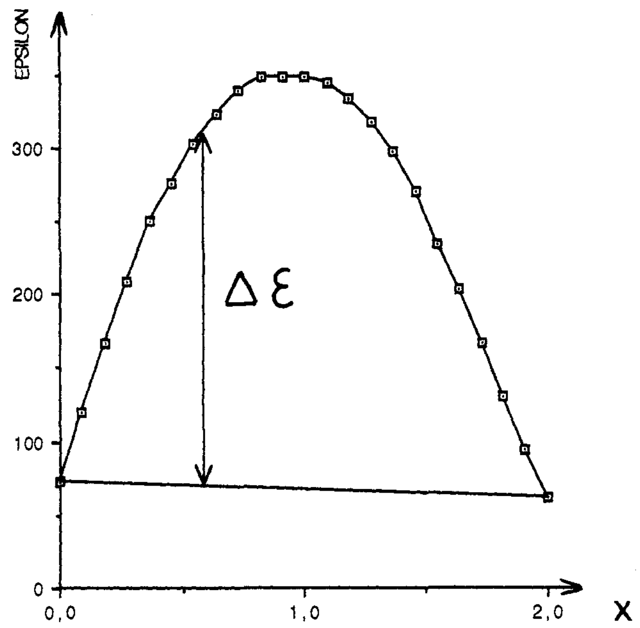

Figure 1. Example of a titration curve: apparent extinction coefficient in the near-IR plotted as a function of the number of electrons (x) for **Ru–2–Ru**. $\Delta\epsilon$ is the excess extinction coefficient, which is proportional to the concentration of the mixed-valence species.

To check that no iodine fixation on the double bonds has interfered, a control experiment was performed using an electrochemical oxidation in water on a platinum electrode on **Ru–2–Ru**. During an oxidation at +200 mV vs SCE, the same sequence of spectra was observed as during the chemical oxidation and a return reduction at −100 mV gave back the original species. Since, furthermore, the oxidation by iodine is instantaneous, we can safely state that no iodine addition occurs under our experimental conditions.

Once the corrected spectrum was obtained, band deconvolution was performed to separate the intervalence band from the nearby metal to ligand charge-transfer transition. The relevant part of the spectrum was fitted to the expression

$$\epsilon = \bar{\nu}A_1 \exp(-0.6914(\bar{\nu} - \bar{\nu}_1)^2/\Delta_1^2) + \bar{\nu}A_2 \exp(-0.6914(\bar{\nu} - \bar{\nu}_2)^2/\Delta_2^2) \qquad (3)$$

using a least-squares minimization procedure. Here A_i, $\bar{\nu}_i$, and Δ_i are respectively the amplitude, position, and half-width at half-maximum for band i (i = 1, 2). An example of such deconvolution is presented on Figure 2.

Uncertainties were estimated by repeating the titration experiments and also modifying the spectral fit parameters until the experimental and calculated curves differ appreciably.

Finally, the effective coupling V_{ab} was computed by[6,7]

$$V_{ab} = 2.05 \times 10^{-2}(\epsilon_{max}\bar{\nu}_{max}\Delta\bar{\nu}_{1/2})^{1/2}/R_{MM} \qquad (4)$$

where V_{ab} is the coupling (in cm^{-1}), ϵ_{max} is the maximum extinction coefficient, $\bar{\nu}_{max}$ is the band position in cm^{-1}, $\Delta\bar{\nu}_{1/2}$ is the full width at half-maximum (cm^{-1}), and R_{MM} is the metal–metal distance in Å. The uncertainty on V_{ab} was found to come essentially from the uncertainties on ϵ_{max} and on $\Delta\bar{\nu}_{1/2}$. A typical calculation gave in the case of **Ru–2–Ru** ±8% on ϵ_{max} (of which 4% came from the titration experiment and spectral simulation and 4% from the uncertainty on K_c) and ±6% on $\Delta\bar{\nu}_{1/2}$. The final uncertainty was in this case ±7% on V_{ab}.

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(7) This simple approach for calculating the electronic coupling from spectroscopic data has been questioned in recent papers. See for instance: Westmoreland, T. D.; Wilcox, D. E.; Baldwin, M. J.; Mims, W. B.; Solomon, E. I. *J. Am. Chem. Soc.* **1989**, *111*, 6106. Dong, Y.; Hupp, J. T. *Inorg. Chem.* **1992**, *31*, 3170. Salaymeh, F.; Berhane, S.; Yusof, R.; de la Rosa, R.; Fung, E. Y.; Matamoros, R.; Lau, K. W.; Zheng, Q.; Kober, E. M.; Curtis, J. C. *Inorg. Chem.* **1993**, *32*, 3895. Note that a more sophisticated method has been subsequently described by Reimers and Hush.[4,5] But in this later method, the separation between experiment and theory is less clear than in the previous one. In addition, it can be expected that the former Hush treatment applies reasonably well for the present systems where the electronic coupling is small. Thus we have used the former Hush method, which is simple, easily applicable to all compounds, and allows comparisons. A copy of the experimental spectra is available on request to J.-P.L. for testing other extraction methods.

(8) Takahashi, K.; Nihira, T.; Akiyama, K.; Ikegami, Y.; Fukuyo, E. *J. Chem. Soc., Chem. Commun.* **1992**, 620.

(9) Takahashi, K.; Nihira, T. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1855.

Table 1. Intervalence Transitions and Metal–Metal Couplings

compd	K_c	$\bar{\nu}_{IVT}$[a] (cm^{-1})	ϵ_{IVT}[b] (mol^{-1}·L·cm^{-1})	$\Delta\bar{\nu}_{1/2}$[c] (cm^{-1})	R_{MM}[d] (Å)	V_{ab}(exptl)[e] (cm^{-1})	V_{ab}(exptl) (eV)	V_{ab}(calc)[f] (eV)
Ru–2–Ru	10 ± 2	10 130 ± 50	660 ± 55	5200 ± 300	15.8	240 ± 17	0.030 ± 0.002	0.036
Ru–3–Ru	10 ± 2	10 700 ± 50	620 ± 55	6000 ± 400	18.1	220 ± 17	0.027 ± 0.002	0.031
Ru–4–Ru	9 ± 2	10 800 ± 50	550 ± 55	5400 ± 400	20.6	180 ± 16	0.022 ± 0.002	0.025
Ru–2–Ru (D_2O)	11 ± 2	10 200 ± 50	740 ± 55	5340 ± 300	15.8	260 ± 17	0.032 ± 0.002	0.036
Ru–3–Ru (D_2O)	10 ± 2	10 900 ± 50	640 ± 55	6000 ± 400	18.1	230 ± 17	0.028 ± 0.002	0.031
Ru–4–Ru (D_2O)	9 ± 2	11 000 ± 50	630 ± 55	5700 ± 400	20.6	200 ± 16	0.024 ± 0.002	0.025
Ru–BPF–Ru	50 ± 2	10 080 ± 10	520 ± 12	5515 ± 200	13.7	254 ± 7	0.0315 ± 0.001	0.038
Ru–BPTh–Ru	14 ± 2	10 151 ± 10	410 ± 20	6610 ± 300	14.5	240 ± 11	0.030 ± 0.001	0.035

[a] Position of the intervalence transition, from deconvolution. [b] Extinction coefficient of the intervalence transition. [c] Full width at half-maximum for the intervalence transition. [d] Metal–metal distance, from molecular models. [e] From eq 4. [f] From ref 17 for **Ru–2–Ru**, **Ru–3–Ru**, and **Ru–4–Ru**.

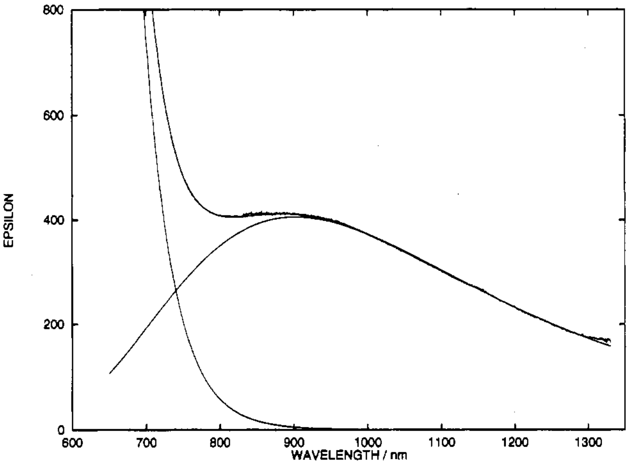

Figure 2. Example of a deconvolution between the intervalence transition and a charge-transfer transition for **Ru–BPTh–Ru** using eq 3.

Results and Discussion

Dipyridylpolyenes as Bridging Ligands. During the redox titration starting from the fully reduced species, the metal-to-ligand charge-transfer band usually located near 550 nm decreases continuously and disappears for 2 equiv of oxidant/mol. In the near-infrared, the intervalence band grows until 1 equiv/mol and then decays. The variation of the optical density in the near-infrared versus the number of added equivalents can be used to determine K_c, according to eq 2.

The K_c values determined from the titration procedure are very similar (see Table 1) although the metal–metal distance varies appreciably between **Ru–2–Ru** and **Ru–4–Ru**. The uncertainty on K_c is rather large, so that the actual K_c variation could be greater than indicated. A simple semi-empirical model has been proposed by Reimers and Hush[4] yielding the formula

$$K_c = 4 \exp(1/\epsilon r_{MM} kT) \qquad (5)$$

where ϵ is the dielectric constant and r_{MM} is the metal–metal distance. Thus a plot of ln K_c versus $1/r_{MM}$ should be linear (Figure 3) and the limiting value of K_c for $r_{MM} \rightarrow \infty$ should be 4, in agreement with statistical arguments. Figure 3 shows the measured and calculated K_c values (from eq 5 with $\epsilon = 31$ as suggested in ref 4). Fortunately the uncertainty on experimental values has only a minor influence on the final corrected extinction coefficient of the mixed-valence species. This comes from the fact that the proportion P of mixed-valence species at half-oxidation, which is given by

$$P = [\text{II–III}]/C_{\text{tot.}} = K_c^{1/2}/(2 + K_c^{1/2}) \qquad (6)$$

varies slowly with K_c in the considered domain. Thus for K_c varying between 8 and 12, P varies only between 0.58 and 0.63.

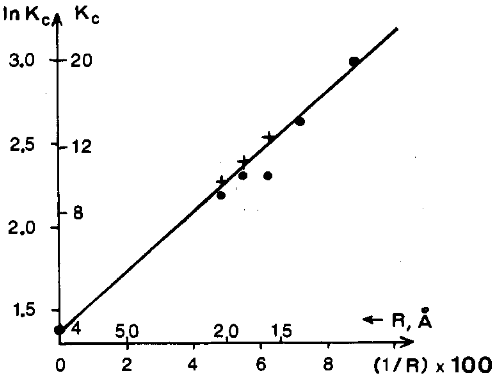

Figure 3. Plot of ln K_c as a function of $1/R_{MM}$, where R_{MM} is the metal–metal distance. The statistical limit corresponds to $R_{MM} \rightarrow \infty$ and $K_c \rightarrow 4$. Key: ●, experimental values (from ref 2 for n = 0 and 1; from this work for n = 2–4); +, theoretical values according to eq 5.

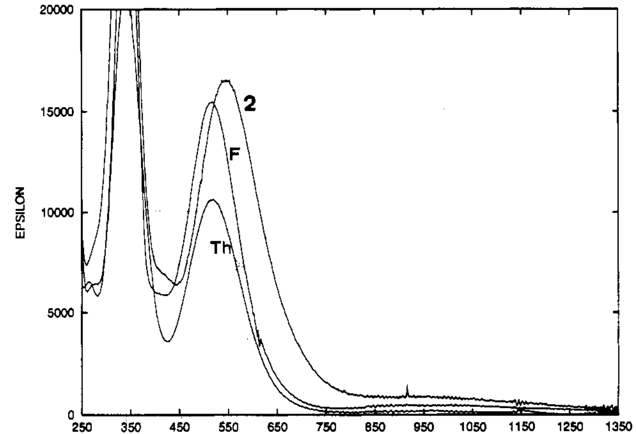

Figure 4. Corrected spectra of mixed-valence compounds in normal water. Charge-transfer transitions occur near 550 nm, while intervalence transitions are the weak and broad bands extending from 750 to 1350 nm. Key: 2, **Ru–2–Ru**; F, **Ru–BPF–Ru**; Th, **Ru–BPTh–Ru**.

The determination of K_c allows the calculation of corrected spectra (Figure 4). Then the deconvolution is performed by assuming Gaussian profiles for both the metal-to-ligand charge-transfer band and the intervalence band. Satisfactory agreement was obtained with the experimental data (see Figure 2). The results of spectral simulations are gathered on Table 1. Intervalence bands for the five compounds are reproduced on Figure 5.

The spectra of the fully oxidized species of **Ru–3–Ru** and **Ru–4–Ru** revealed a curious feature made of several closely weak bands (see Figure 6) in the 700–1100-nm range, as also observed by Curtis.[10] The energy separation of the bands is of the order of 1400 cm^{-1}, and they move toward lower energies when the number of double bonds increases. Several possible assignments have been considered: (i) d–d bands of ruthenium(III) corresponding to $t_{2g} \rightarrow e_g$ transitions, where this seems unlikely because they are usually estimated to occur near 460 nm in pentaammineruthenium(II) systems[11] and thus should appear at higher energies with ruthenium(III); (ii) "intra t_{2g}" bands due to the

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(10) Curtis, J. C. Private communication.

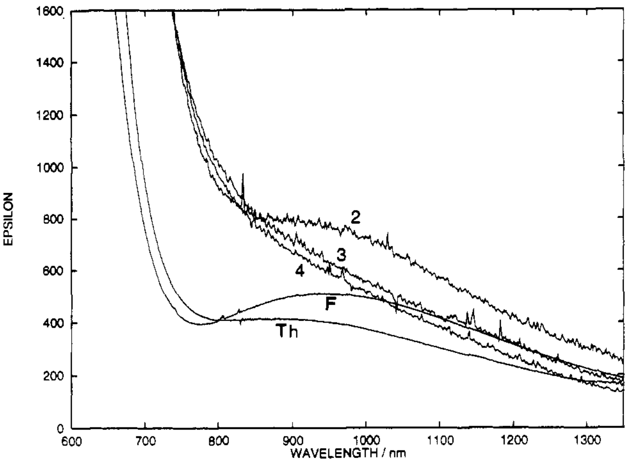

Figure 5. Intervalence bands in water. Key: 2, **Ru–2–Ru**; 3, **Ru–3–Ru**; 4, **Ru–4–Ru**; F, **Ru–BPF–Ru**; Th, **Ru–BPTh–Ru**. Note that **Ru–3–Ru** and **Ru–4–Ru** present neither a maximum nor a shoulder corresponding to the intervalence transition. However the presence of the intervalence transition is shown by the profile analysis on the tail of the metal-to-ligand charge-transfer transition.

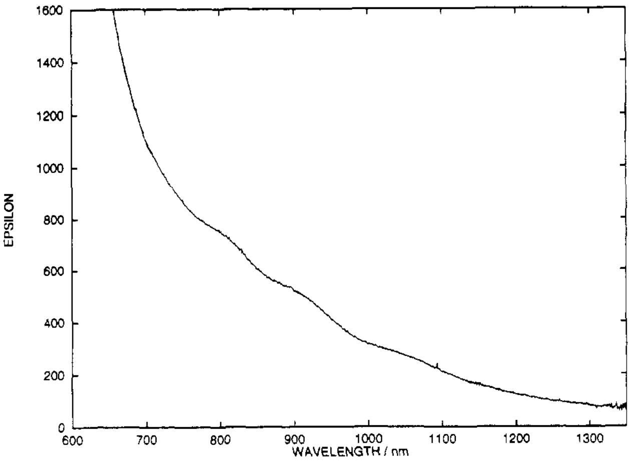

Figure 6. Small bands of ruthenium(III) observed in the fully oxidized form of **Ru–4–Ru**.

lower-than-octahedral symmetry, where this is also unlikely because such bands are anticipated near 2500 cm^{-1} (i.e. 4000 nm) according to Krogh-Jespersen *et al.*[12] or 1900 cm^{-1} (5200 nm) according to Hupp and Meyer;[13] (iii) ligand-to-metal charge-transfer bands, where this would explain their displacement to the longer wavelength region with the number of double bonds, which is parallel to the displacement of the more intense bands observed near 500–550 nm in these fully oxidized complexes. Let us recall that these 500–550-nm bands are assigned to ligand-to-metal charge-transfer transitions.[4]

So in this last hypothesis, which we consider as the most likely, the separation observed on the weak bands would correspond to a vibrational structure due to the dipyridylpolyene ligand (note that these features are not observed with dipyridylthiophene and -furan).

In view of the extension of intervalence bands toward the infrared, some experiments have also been performed in D_2O. This expands the spectral limit from 1350 nm (onset of water absorption) to 1700 nm. It is thus possible to observe the complete low-energy profile of the intervalence absorption. However the band parameters are very similar to the ones observed in normal water (see Table 1).

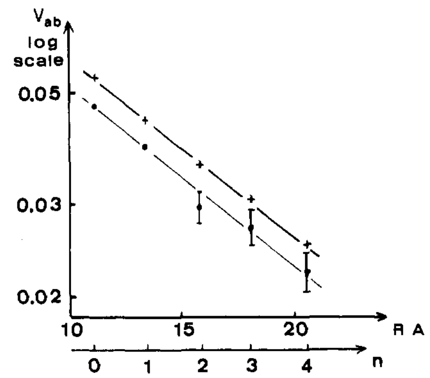

Figure 7. Variation of the metal–metal coupling V_{ab} (in logarithmic scale) as a function of the metal–metal distance. Key: +, calculated values, from extended Hückel; ●, experimental values, with a tentative straight line corresponding to an exponential decay. Deviations to an exponential decay are nevertheless possible due to the uncertainty on V_{ab}.

Table 2. Spectral and Electrochemical Characteristics of **Ru^{II}–BPF–Ru^{II}** and **Ru^{II}–BPTh–Ru^{II}**

compd	UV-vis spectral data in water: λ_{max}, nm (ϵ_{max}, mol^{-1}·L·cm^{-1})	electrochemical peak potentials[a] (V) E_{pa}	E_{pc}
Ru^{II}–BPF–Ru^{II}	327 (20 500),[b] 517 (26 500)[c]	0.170	0.002
Ru^{II}–BPTh–Ru^{II}	330 (18 400),[b] 515 (21 000)[c]	0.201	0.068

[a] Versus SCE. Solvent is DMF containing 0.1 M tetrabutylammonium hexafluorophosphate. E_{pa} is the anodic peak potential, and E_{pc} the corresponding cathodic peak. [b] Ligand π–π^* band. [c] Metal-to-ligand charge transfer.

Electronic coupling parameters V_{ab} were finally obtained through eq 4 and are reported in Table 1. The difference between values obtained in normal water and in D_2O is considered to be nonsignificant, because it is lower than the estimated error. When ln V_{ab} is plotted as a function of the metal–metal distance (Figure 7), the *general trend* is a linear decrease, corresponding to an exponential decay for V_{ab}. However *the uncertainty is rather large and increases with n, which could hide small deviations to an exponential variation.* These deviations have been in particular predicted by Joachim[14] and also by Hush.[4,15] Considering the present state of the experiment, and taking into account the difficulties due to extensive overlap between the bands, it is impossible to make conclusions about the exact character (exponential or not) of the decay.

Dipyridylfuran and -thiophene as Bridging Ligands. The binuclear complexes of these ligands were obtained in the usual way.[1] Spectral and electrochemical characteristics are gathered in Table 2. They are very similar to the ones of **Ru–2–Ru**.

Cyclic voltammograms in DMF of the Ru^{II}–BPF–Ru^{II} and the Ru^{II}–BPTh–Ru^{II} complexes exibit single reversible waves without indications of splitting in two monoelectronic waves. However, as for previous compounds,[1] the titration experiment shows that a mixed-valence compound is formed during oxidation. Curiously, the BPF system gave a surprisingly high K_c value (*ca.* 50 instead of 10–14), showing some extra stability for the mixed-valence species.

The general behavior upon oxidation is the same as with dipyridylpolyenes. Intervalence bands were also observed, as a clearly defined maximum in the case of dipyridylfuran, while only a shoulder is exhibited by the dipyridylthiophene compound. However, in both cases, it is possible to perform a relatively accurate deconvolution. The V_{ab} values are very similar to the one of **Ru–2–Ru**. When comparisons are made with dipy-

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(11) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 7213. Durante, V. A.; Ford, P. C. *Inorg. Chem.* **1979**, *18*, 588.

(12) Krogh-Jespersen, K.; Westbrook, J. D.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1987**, *109*, 7025.

(13) Hupp, J. T.; Meyer, T. J.; *Inorg. Chem.* **1987**, *26*, 2332.

(14) Joachim, C. *Chem. Phys.* **1987**, *116*, 339.

(15) Reimers, J. R.; Hush, N. S. In *Molecular Electronics-Science and Technology*; Aviram, A., Ed.; United Engineering Trustees: New York, 1989; p 339.

ridylpolyenes, it appears that the main reason for the increased resolution of the intervalence band comes from the sharper profile of the metal-to-ligand charge-transfer band in the case of the dipyridylfuran compound (see Figure 4). The difference between dipyridylpolyene and dipyridylheterocycles could be due to the more rigid and coplanar conformations of the latter ligands. This is suggested by the very strong fluorescence emission observed in the viologen type *N,N'*-dimethyl derivatives of dipyridylfuran and dipyridylthiophene,[8] whereas no fluorescence emission is observed in those of dipyridylpolyenes. Interestingly, the experimentally determined quantum yield is highest in the *N,N'*-dimethyl derivative of dipyridylfuran.[8] Strong fluorescence is usually an indication of a rigid and coplanar structure. In the present case, a consequence of rigidity would be to narrow the distribution of twisting angles and thus to sharpen the electronic transitions.

A related class of bridging ligands has been studied by Kim and Lieber, who have described intervalence transitions between pentaammineruthenium groups connected through dipyridylbenzene and dipyridylbiphenyl.[16] In contrast with dipyridylheterocycles, their intervalence spectra are particularly weak and appear only as shoulders on the tail of the charge-transfer transition. These unfavorable characteristics could be explained by the two following factors: (i) coplanarity is more difficult to achieve in dipyridylbenzene due to the steric interaction between biphenylic ortho hydrogen atoms and (ii) the phenylene group exhibiting a strong aromaticity is unfavorable as a mediator since its conjugative interaction with terminal pyridine rings would be realized at the expense of its own aromaticity. By contrast, the present heterocycles (especially furan) are less aromatic and thus are more able to interact with the rest of the molecule.

Theoretical Calculations

Theoretical calculations of V_{ab} couplings are possible by the extended Huckel method, as already described for the dipyridylpolyenes.[17] The obtained values are in relatively good agreement with the experimental ones, the maximum discrepancy being around 12%. On the other hand, our theoretical values are markedly higher than the computed values of Reimers and Hush,[4] the difference ranging from 15% for $n = 2$ to 40% for $n = 4$. Thus although the extended Huckel method is a rather crude one, it reproduces satisfactorily the general trend.

For dipyridylfuran and dipyridylthiophene complexes also, a satisfactory agreement is obtained, although the computed values are slightly above the experimental ones.

Conclusion

Intervalence transitions provide an easy way to characterize intramolecular electron transfer in binuclear coordination complexes, although the accuracy is not good enough with dipyridylpolyenes to test theoretical models about the decay of electronic interaction with distance. In other respects, it appears that heterocycles are good relay groups to mediate the electronic interaction and are equivalent to two double bonds, in agreement with chemical intuition. They present however two distinct advantages over polyenes: a better chemical stability and a better resolution of the intervalence transition. This last point is due to subtle changes in the profile of the metal-to-ligand charge-transfer transition (which incidentally is not the same in the fully reduced form and in the mixed-valence form).[18]

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[16] Kim, Y.; Lieber, C. M. *Inorg. Chem.* **1989**, *28*, 3990.

[17] Joachim, C.; Launay, J.-P.; Woitellier, S. *Chem. Phys.* **1990**, *147*, 131.

[18] Another factor influencing the resolution of intervalence transistions is the nature of the terminal groups. Thus ruthenium–bis(terpyridyl) end groups give rise to intervalence transitions at markedly higher wavelengths (1100–1500 nm), facilitating the observation of the complete band profile: Collin, J.-P.; Lainé, Ph.; Launay, J.-P.; Sauvage, J.-P.; Sour, A. *J. Chem. Soc., Chem. Commun.* **1993**, 434.