that this aspect of the previous interpretations should be reevaluated. Moreover, while planar CuCl$_4^{2-}$ is unusual because of the very low energy of the intensity-inducing β_{2u} mode, the present results suggest that caution should be exercised in the application of the simple model of vibronic coupling in other systems.

There has recently been considerable interest in the temperature-dependent EPR spectra observed for various Cu(II) complexes,[17] and the CuCl$_4^{2-}$ ion has been proposed as a model for biologically important systems of this kind.[18] It has been suggested that the unusual behavior of these systems may be caused by a highly anharmonic potential surface in the ground state of the complexes.[17,19] The present studies suggest that the anomalous temperature dependence of the optical spectrum of planar CuCl$_4^{2-}$ is strongly influenced by the form of the excited-state potential surfaces, and we are considering the implications that this may have on the interpretation of temperature-dependent EPR parameters.

Acknowledgment. The Australian Research Grants Scheme is thanked for financial assistance, and R.G.M. and M.J.R. are grateful for grants from the University of Tasmania and the Commonwealth of Australia, respectively.

---

(17) Bacci, M.; Cannistraro, S. *Chem. Phys. Lett.* **1987**, *133*, 109.

(18) Solomon, E. I.; Hare, J. W.; Dooley, D. M.; Dawson, J. H.; Stephens, P. J.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 168.

(19) Bacci, M. *Chem. Phys.* **1984**, *88*, 39.

Contribution from the Laboratoire de Chimie des Métaux de Transition, Université Pierre et Marie Curie, Paris, France, and Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

Intervalence Transfer in Pentaammineruthenium Complexes of α,ω-Dipyridyl Polyenes

S. Woitellier,[†] J. P. Launay,[*,†] and C. W. Spangler[*,‡]

Received June 3, 1988

Binuclear complexes containing the pentaammineruthenium(II) moiety linked to α,ω-dipyridyl polyenes have been prepared. The systems investigated have two, three, or four conjugated double bonds connecting the pyridyl moieties, and the metal-metal distance ranges from 15.8 to 20.6 Å. The electrochemical and spectroscopic properties of the complexes are described. Progressive oxidation gives rise to mixed-valence compounds exhibiting an intervalence transition in the near-IR region. The best resolution of these intervalence transitions with respect to the nearby charge-transfer transition is realized with nitrobenzene as solvent. The electronic coupling parameter is calculated from the intensity of the intervalence band and is shown to decrease only by ca. 30% when going from two to four double bonds.

Introduction

The experimental and theoretical study of long-distance electron transfer is a very active current research topic. The consequences of this process are of crucial importance in domains such as biology,[1] solid-state chemistry,[2] inorganic reaction mechanisms,[3] and finally the emerging field of molecular electronics.[4] In particular, the question of the rate of decay of the electronic interaction between the two redox sites as a function of distance has received considerable attention.[5-9]

In the course of a general program devoted to molecular electronics, we have undertaken the synthesis of new model systems in which two redox sites are linked by a conjugated pathway.[10] The aims of this investigation are the following.

(i) We wish to show the possibility of long-distance electron transfer in or near the ground state. This would lead to the synthesis of "molecular wires" allowing the intramolecular propagation of electrons between a donor and acceptor site. In this respect, Lehn and co-workers have recently synthesized "caroviologens" with redox sites separated by a long conjugated chain.[11]

(ii) We wish to investigate the possibility of "molecular switching" by a conformational change. As a prerequisite for this, the synthesis of sufficiently long bridging ligands appears necessary in order to ensure that the electron transfer really proceeds through bonds and not through space. The electron-transfer rate will then be influenced by the properties of the intramolecular medium and could probably be changed by a variation in the geometrical or energetic properties of the system.

Here we describe the electron-transfer ability of α,ω-dipyridyl polyenes of the general type py(CHCH)$_n$py (py = pyridyl) in which $n = 2$–4. In the following, these ligands will be denoted **2**, **3**, and **4**, respectively. The metal sites coordinated to the pyridine ends of these ligands are Ru(NH$_3$)$_5^{2+/3+}$ moieties, giving binuclear complexes denoted as $\mathbf{2}_{\mathrm{Ru}}$, $\mathbf{3}_{\mathrm{Ru}}$, and $\mathbf{4}_{\mathrm{Ru}}$, respectively (see Figure 1). According to the pioneering work of Taube,[12] Meyer,[13] and others, pentaammineruthenium groups are particularly well suited for this purpose. Indeed, the two oxidation states 2+ and 3+ are stable and are easily interconverted at a reasonable redox potential. In addition, with NH$_3$ as ancillary ligands, ruthenium(II) is a strong π donor and interacts efficiently with the π acceptor bridging ligand. This is a favorable factor for the transmission of the electronic interaction.

The present systems thus represent a development of the work already performed by Sutton and Taube[14,15] and Meyer and coworkers[16] using 4,4′-bipyridine (**0**) and dipyridylethylene (**1**) bridging ligands.

[†] Université Pierre et Marie Curie.

[‡] Northern Illinois University.

(1) Scott, R. A.; Mauk, A. G.; Gray, H. B. *J. Chem. Educ.* **1985**, *62*, 932. Isied, S. S. *Prog. Inorg. Chem.* **1984**, *32*, 443.

(2) Mikkelsen, K. V.; Ratner, M. A. *Chem. Rev.* **1987**, *87*, 113.

(3) Fischer, H.; Tom, G. M.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 5512.

(4) *Molecular Electronic Devices*; Carter, F. L., Ed.; Marcel Dekker: New York, 1982. *Molecular Electronic Devices II*; Carter, F. L., Ed.; Marcel Dekker: New York, 1987.

(5) Larsson, S. *Chem. Phys. Lett.* **1982**, *90*, 136. Larsson, S. *Discuss. Faraday Soc.* **1982**, *74*, 390.

(6) (a) Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135. (b) Oevering, H.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 3258.

(7) Newton, M.; Sutin, N. *Annu. Rev. Phys. Chem.* **1984**, *35*, 437.

(8) Beratan, D. N.; Hopfield, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 1584.

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

(10) Launay, J. P.; Woitellier, S.; Sowinska, M.; Tourrel, M.; Joachim, C. In *Proceedings of the 3rd International Symposium on Molecular Electronic Devices*; Carter, F. L., Wohltjen, H., Eds.; North-Holland: Amsterdam, in press.

(11) Arrhenius, T. S.; Blanchard-Desce, M.; Dvolaitzky, M.; Lehn, J. M.; Malthete, J. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 5355.

(12) Taube, H. In *Tunneling in Biological Systems*; Chance, B., Marcus, R. A., De Vault, D. C., Schrieffer, J. R., Frauenfelder, M., Sutin, N., Eds.; Academic Press: New York, 1979; p 173.

(13) Powers, M. J.; Callahan, R. W.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1976**, *15*, 894.

(14) Sutton, J. E.; Sutton, P. M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 1017.

(15) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125.

(16) Hupp, J. T.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 2332. Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1289.

0020-1669/89/1328-0758$01.50/0

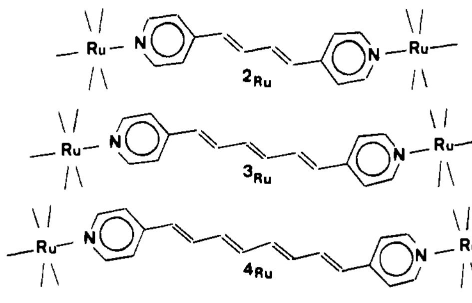

Figure 1. Schematic structures of the complexes investigated.

Experimental Section

Proton and carbon NMR spectra were determined as solutions in $CDCl_3$ ($SiMe_4$ as internal reference) with an IBM 200 spectrometer. All melting points are uncorrected.

UV-visible-near-IR spectra were recorded with a Beckman 5240 spectrophotometer. Cyclic voltammetry was performed with Tacussel equipment. The solvent was dimethylformamide containing 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte, and the working electrode was a platinum wire. The reference electrode was an aqueous saturated calomel electrode equipped with a double-frit system.

(*E*,*E*)-1,4-Bis(4-pyridyl)-1,3-butadiene (2). Dipyridylbutadiene was prepared by a modification of the method described by Hunig et al.[17] 4-Pyridylcarbinol was converted to (bromomethyl)-4-pyridinium bromide and then to triphenyl(4-picolyl)phosphonium bromide. The Wittig condensation was then performed with glyoxal. Following recommendations by Hunig, it is essential to use the hydrated trimer with empirical formula $(C_2H_2O_2)_3{\cdot}2H_2O$. Glyoxal dihydrate (2.8 g, 40 mmol, from Schuchardt) in 20 mL of DMSO was mixed with a solution of triphenyl(4-picolyl)phosphonium bromide (38.28 g, 88 mmol) in 200 mL of absolute ethanol. After the mixture was heated several minutes at 70 °C to depolymerize glyoxal, 8.64 g of methylsodium (160 mmol) was added and the mixture was refluxed overnight. The formation of dipyridylbutadiene can be checked by the appearance of characteristic bands in the ultraviolet spectrum (see below). The solution was then cooled, and a crude product was precipitated by addition of 20 mL of absolute ethanol saturated with HCl. The orange solid was collected, washed with diethyl ether, and redissolved in 315 mL of 1 N aqueous HCl, and the solution was refluxed 15 min in the presence of activated charcoal. After filtration while hot, the solution was neutralized by 10 N NaOH. Precipitation occurred near pH 7. The solid was filtered, washed with water, and recrystallized twice in a methanol-water (1:1) mixture, giving beautiful light beige needles. The yield was 4.16 g (50% with respect to glyoxal); mp 163 °C (lit.[17] mp 164-165 °C). Anal. Calcd for $C_{14}H_{12}N_2{\cdot}0.5CH_3OH$: C, 77.67; H, 6.25; N, 12.50. Found: C, 77.48; H, 5.98; N, 12.84.

The crystal structure has been solved and will be reported in a later publication.[18] It confirms the presence of half a methanol molecule of crystallization.

(*E*,*E*,*E*)-1,6-Bis(4-pyridyl)-1,3,5-hexatriene (3). A solution of potassium *tert*-butoxide (12.1 g in 200 mL of glyme) was added dropwise to a solution of tetraethyl ((*E*)-2-butene-1,4-diyl)diphosphonate (16.4 g, 0.05 mol) and pyridine-4-carboxaldehyde (10.70 g, 0.10 mol) in 100 mL of glyme at room temperature. The reaction was quite exothermic, and the reaction temperature was controlled by the rate of addition to 60 °C or less. After the addition of the base was complete, the resulting mixture was stirred at room temperature for 16 h. Cold water (ca. 300-400 mL) was added and the product isolated by vacuum filtration (3.5 g, 30% crude yield) and recrystallized from acetone (2.3 g, 19%): mp 196-198 °C (lit.[17] mp 197-198 °C); ^1H NMR δ 6.5-6.7 (m, 4 vinyl H), 7.0-7.15 (m, 2 vinyl H), 7.2-7.4 (m, 4 β-ring H), 8.5-8.7 (m, 4 α-ring H); ^{13}C NMR δ 120.6, 131.3, 132.7, 134.9, 144.1, 150.2. Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.05; H, 5.98; N, 11.96. Found: C, 81.92; H, 6.00; N, 11.92.

(*E*,*E*,*E*,*E*)-1,8-Bis(4-pyridyl)-1,3,5,7-octatetraene (4). A solution of potassium *tert*-butoxide (12.1 g, in 200 mL of glyme) was added dropwise to a solution of tetraethyl ((*E*,*E*)-2,4-hexadiene-1,6-diyl)diphosphonate (17.5 g, 0.05 mol) and pyridine-4-carboxaldehyde (10.70 g, 0.10 mol) in 100 mL of glyme at room temperature. The reaction was worked up in the manner described above for 1,6-bis(4-pyridyl)-1,3,5-hexatriene, yielding **4** (5.4 g, 42%), which was then recrystallized from toluene/DMF (3.96 g, 30%): mp 217 °C; ^1H NMR δ 6.4-6.6 (m, 6 vinyl H), 7.0-7.15 (m, 2 vinyl H), 7.2-7.4 (m, 4 β-ring H), 8.5-8.7 (m, 4 α-ring H); ^{13}C NMR δ 120.6, 130.6, 133.1, 133.9, 135.6, 144.3, 150.2. Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.20; N, 10.76. Found: C, 82.88; H, 6.35; N, 10.92.

Binuclear Pentaammineruthenium(II) Complexes. The binuclear complexes were prepared by the interaction of $[(NH_3)_5Ru(H_2O)]^{2+}$ with the corresponding ligand in a methanol-acetone mixture. The salt $[(NH_3)_5Ru^{II}(H_2O)](PF_6)_2{\cdot}H_2O$ was prepared according to the following adaptation of the method described by Lavallee and Fleischer.[19] A 50-g amount of granulated zinc (20 mesh) was converted to zinc amalgam. A suspension of 2 g (6.56 mmol) of $[Ru^{III}(NH_3)_5Cl]Cl_2{\cdot}{}^2/_3H_2O$ (Johnson Matthey) in 100 mL of deaerated water was acidified with ca. 0.5 mL of pure trifluoromethanesulfonic acid. The zinc amalgam was introduced and the mixture stirred under argon until dissolution of the ruthenium compound, which was generally complete after a few minutes. A yellow, almost transparent solution was obtained, which was filtered in a Schlenk tube to eliminate the remaining amalgam, as well as some unreacted ruthenium species. In some cases, the complete dissolution was never observed; under such circumstances, it is essential not to wait more than 15 min, since complex hydrolysis reactions involving the loss of ammonia begin to develop. The precipitation was performed with 3 g of solid ammonium hexafluorophosphate. The product was washed with deaerated water and dried under vacuum. The yield was 1.2 g (36%). Although this reaction has been described several times, the obtainment of a pure product proved difficult. Thus, control of its purity was systematically performed by using cyclic voltammetry (single wave at -0.18 V in DMF) and by UV-visible spectroscopy in acetone (λ_{max} 362 nm, ϵ = 2800 M^{-1} cm^{-1}). An impurity was sometimes detected by an extra wave at -0.45 V, which could be eliminated by washing successively with a 3:1 ethanol-water mixture, then pure ethanol, and finally ether. The product was obtained as a yellow powder, which can be kept for 1 month under argon at -20 °C.

For the synthesis of complexes, a typical experiment is described below, in the case of $\mathbf{2}_{Ru}$. All reactions were carried out in Schlenk tubes with dried and degassed solvents. Thus, 4.15 g (8 mmol) of $[(NH_3)_5Ru(H_2O)](PF_6)_2{\cdot}H_2O$ was dissolved in 20 mL of degassed acetone while 0.675 g of dipyridylbutadiene (3.24 mmol) was dissolved in 20 mL of methanol. The methanol solution was then transferred to the acetone solution by using a cannula. After it was stirred 6 h in the dark, the solution was filtered and precipitation induced by transferring it to 300 mL of diethyl ether. The resulting solid was washed twice by decantation with ether, and finally the suspension was dried on a vacuum line, yielding 3.15 g of crude product. Cyclic voltammetry in DMF then showed the presence of impurities (waves at -0.2 and -0.35 V, while the main wave due to the product occurred near +0.08 V). They were eliminated by repeated washings with water. The final yield was 1 g (26% with respect to the ligand). Anal. Calcd for $[Ru(NH_3)_5$-**2**-$Ru(NH_3)_5](PF_6)_4$: C, 14.47; H, 3.62; N, 14.47; Ru, 17.42; P, 10.68. Found: C, 14.18; H, 3.75; N, 14.11; Ru, 17.41; P, 10.73.

The other complexes were prepared by the same general procedure, except that, owing to the lower solubilities of the ligands in methanol, they were carefully ground before use and transferred as suspensions. Despite this, the reaction occurred as above; filtration of the solution after reaction yielded only a small residue of unreacted ruthenium species. Anal. Calcd for $[Ru(NH_3)_5$-**3**-$Ru(NH_3)_5](PF_6)_4{\cdot}CH_3COCH_3$: C, 18.32; H, 4.02; N, 13.50; P, 9.96. Found: C, 18.76; H, 4.95; N, 12.04; P, 9.73. Calcd for $[Ru(NH_3)_5$-**4**-$Ru(NH_3)_5](PF_6)_4{\cdot}4H_2O$: C, 16.82; H, 4.20; N, 13.08; P, 9.65. Found: C, 16.79; H, 4.16; N, 11.71; P, 9.26.

As already mentioned by others,[20] nitrogen analyses are sometimes defective, but the purity of the products is shown by cyclic voltammetry.

Oxidation Procedure. Oxidation to generate the mixed-valence ruthenium(II)-ruthenium(III) species was performed either in D_2O (0.1 M in DCl), using a solution of bromine in D_2O as oxidant, or in nitrobenzene. In this last case, the oxidizing agent was $[Fe(bpy)_3](PF_6)_3$ prepared according to ref 21. The oxidation was monitored by following the optical density in the near-IR region, which first increased and then subsequently decreased as a result of the formation of the mixed-valence species. The maximum optical density was recorded and was used for the calculation of the extinction coefficient after correction for the comproportionation equilibrium.

Results and Discussion

Properties of the Free Ligands. The ligands used here are all-trans isomers. This is shown by their NMR spectra and the strong analogy of their electronic spectra with the ones of the

---

(17) Carsky, P.; Hunig, S.; Stemmler, I.; Scheutzow, D. *Liebigs Ann. Chem.* **1980**, 291.

(18) Gourdon, A.; Woitellier, S.; Launay, J. P. To be submitted for publication.

(19) Lavallee, D. K.; Fleischer, E. B. *J. Am. Chem. Soc.* **1972**, *94*, 2583.

(20) Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40.

(21) Chang, J. P.; Fung, E. Y.; Curtis, J. C. *Inorg. Chem.* **1986**, *25*, 4233.

Table I. Ultraviolet–Visible Spectra in Methanol of the Bridging Ligands

ligand	λ_{max}, nm (ϵ, 10^3 M^{-1} cm^{-1})[a]
2	300 (sh), 314 (45.5), 327 (56.0), 343 (39.7)
3	322 (sh), 338 (54.1), 353 (75.8), 372 (60.5)
4	340 (sh), 360 (63.3), 377 (92.9), 398 (82.0)

[a] sh = shoulder.

Table II. Electrochemical Data for the Free Ligands and for the Binuclear Ruthenium Complexes[a]

ligand	$E_{1/2}$, V	complex	$E_{1/2}$, V	
			Ru	ligand
2	−1.54, −1.80	$\mathbf{2}_{Ru}$	+0.09	−1.39, −1.59[b]
3	−1.46, −1.63	$\mathbf{3}_{Ru}$	+0.07	−1.42[b]
4	−1.44	$\mathbf{4}_{Ru}$	+0.08	−1.33

[a] From cyclic voltammetry; $E_{1/2}$ values are averages of cathodic and anodic peaks and are given vs aqueous SCE. The solvent is DMF. [b] Irreversible wave. The potential given corresponds to the rising portion, at 85% of the peak current.

corresponding all-trans diphenyl polyenes.[22] Finally, this has been directly checked in the case of **2** by the resolution of the crystal structure. Although the quality of this structural determination is not excellent due to pseudosymmetry and the existence of disordered solvent molecules, it shows unambiguously that we are dealing with the *E,E* isomer. The complete structural work will be described in a later publication.[18]

UV–visible spectra of the free ligands exhibit the $\pi\pi^*$ transition with a characteristic fine structure. Wavelengths and extinction coefficients are gathered in Table I. The bands move to higher wavelengths (lower energies) and the extinction coefficients increase when the length of the conjugated system increases.[23]

Cyclic voltammograms generally show two reduction waves between −1.4 and −1.8 V, except in the case of **4**, where these waves are fused together (Table II). According to Hunig et al.,[24] each wave corresponds to a 1e process, and their separation depends upon the electrostatic repulsion between the second added electron and the first. Thus, the separation of waves decreases between **2** and **3**, and for the larger system **4**, this repulsion is so weak that a unique bielectronic wave is observed.

Homovalent Ruthenium(II) Complexes ($\mathbf{2}_{Ru}$, $\mathbf{3}_{Ru}$, $\mathbf{4}_{Ru}$). The homovalent ruthenium(II) binuclear complexes are obtained as PF_6^- salts, exhibiting moderate solubilities in polar organic solvents and water. An interesting qualitative observation is that the solubilities vary in opposite directions with the length of the system: thus, in water the most soluble complex is $\mathbf{2}_{Ru}$, while in nitrobenzene the most soluble is $\mathbf{4}_{Ru}$. (In this last solvent, a sudden variation occurs between $\mathbf{3}_{Ru}$ and $\mathbf{4}_{Ru}$.) This is clearly due to the balance between the hydrophilic character of the terminal pentammineruthenium(II) groups and the hydrophobic character of the central hydrocarbon chain. For *very* long systems (11 conjugated double bonds for instance), this provides an amphiphilic character to the molecule, with the possibility of incorporation in a membrane.[11]

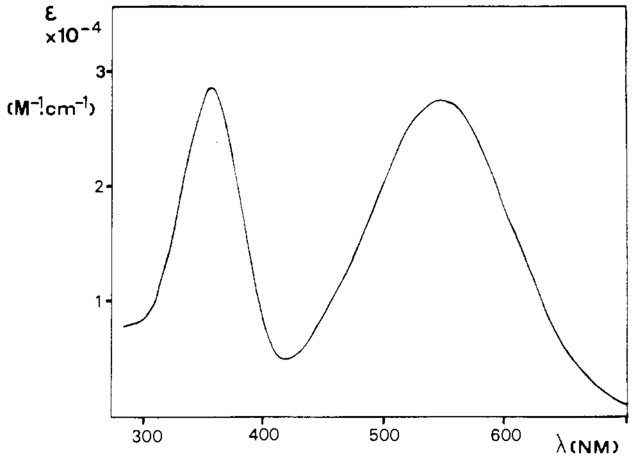

Figure 2. Ultraviolet–visible spectrum of the binuclear complex $\mathbf{3}_{Ru}$ in water.

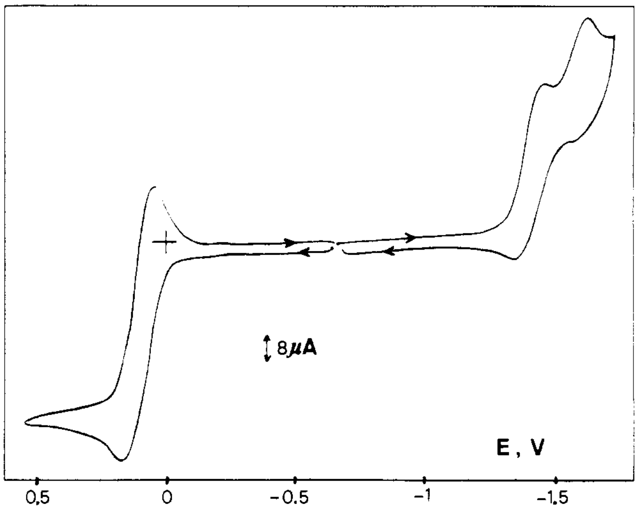

Figure 3. Cyclic voltammetry of the binuclear complex $\mathbf{2}_{Ru}$ in DMF.

Table III. Ultraviolet–Visible Spectra of the Binuclear Ruthenium Complexes in Water and Nitrobenzene

complex	λ_{max}, nm (ϵ, 10^3 M^{-1} cm^{-1})		
	water		nitrobenzene[a]
$\mathbf{2}_{Ru}$	327 (31.4)	545 (33.0)	550 (30.0)
$\mathbf{3}_{Ru}$	353 (30.0)	545 (28.7)	545 (31.2)
$\mathbf{4}_{Ru}$	377 (34.2)	545 (32.2)	545 (35.3)

[a] Ultraviolet bands not recorded in this case, due to solvent absorption.

The UV–visible spectra show the $\pi\pi^*$ ligand transitions near 320–380 nm. The main difference with respect to the spectra of the free ligands resides in the loss of the fine structure. All complexes exhibit also an intense band in the visible region, which is ascribed to a metal-to-ligand charge-transfer transition[25] (see Table III and Figure 2). It is found that the energy of this transition is practically constant for the three different complexes. Thus, there is no dramatic change in the orbital energies when the number of conjugated double bonds increases. The intensity of the transition does not change appreciably when the length of the conjugated ligand increases. This is rather surprising since the expression of the transition moment for a charge-transfer transition involves the donor to acceptor separation. Thus, two explanations can be envisaged: (i) the charge transfer involves an electron transfer from the ruthenium site to the adjacent pyridine ring with almost no contribution from the polyene chain; (ii) the charge transfer really involves the polyene chain, and thus the effective distance increases with *n*, but some compensation occurs because at the same time the electronic interaction and orbital mixing between ruthenium and ligand decrease. The first hypothesis appears unlikely because the position of the charge-transfer band is very different from the case of $[(NH_3)_5Ru(pyridine)]^{2+}$.[26] In addition, we have performed extended Hückel

---

(22) Sandoval, A.; Zechmeister, L. *J. Am. Chem. Soc.* **1947**, *69*, 553. Pinckard, J. H.; Wille, B.; Zechmeister, L. *J. Am. Chem. Soc.* **1948**, *70*, 1938. Lunde, K.; Zechmeister, L. *J. Am. Chem. Soc.* **1954**, *76*, 2308. Zechmeister, L.; Pinckard, J. H. *J. Am. Chem. Soc.* **1954**, *76*, 4144.

(23) Our spectrum for **3** does not agree with the one given in ref 17. Since our spectra show a perfectly regular change with *n* and a great analogy with the case of α,ω-diphenyl polyenes, we believe that the spectrum given in ref 17 is incorrect.

(24) Horner, M.; Hunig, S.; Putter, H. *Electrochim. Acta* **1982**, *27*, 205.

(25) See for instance: Winkler, J. R.; Netzel, T. L.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1987**, *109*, 2381.

(26) Ford, P.; Rudd, F. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187.

calculations which show that, in the present complexes, the LUMO has large contributions coming from the polyene chain.[27] We thus consider the second hypothesis as more likely.

Cyclic voltammetry in dimethylformamide always shows a single oxidation wave, without any sign of splitting (see Table II and Figure 3). Thus, the difference in redox potentials between the Ru^{II}–Ru^{II}/Ru^{II}–Ru^{III} and Ru^{II}–Ru^{III}/Ru^{III}–Ru^{III} couples is below the resolution limit. This is not surprising since the separation of waves in this kind of complexes usually comes from electrostatic effects. In the complex $\mathbf{1}_{Ru}$ studied by Sutton and Taube the separation was already not apparent, and the difference in half-wave potentials was estimated from the comproportionation constant to be near 70 mV.[15] In our longer systems, we can a fortiori assume that the electrostatic interaction between metal sites plays a negligible role and that the sites are oxidized independently of each other. (Incidentally, this does not mean that the electronic coupling between the two sites, which depends upon different structural parameters, vanishes.) Consequently, as far as thermodynamic equilibria are concerned, we shall assume in the following that the comproportionation equilibrium

$$K_c = [Ru^{II}\text{–}Ru^{III}]^2/[Ru^{II}\text{–}Ru^{II}][Ru^{III}\text{–}Ru^{III}]$$

is very near to the statistical limit; i.e., $K_c = 4$. Thus, when half of the total ruthenium has been oxidized in the titration experiment, we shall assume that the solution actually contains 50% of the dimer as mixed-valence species, the remaining being an equimolar mixture of homovalent species (25% of each). This assumption about the value of K_c is supported by the results of Taube and co-workers showing that when the metal–metal distance reaches ca. 12 Å, the comproportionation constant is already near the statistical limit.[14,15,20,28] By comparison, in our complexes, the metal–metal distance ranges from 16 to 20 Å.[29]

The voltammograms also exhibit ligand reduction waves near −1.4 V (Table II and Figure 3). When these waves are compared with the reduction waves of the free ligands, it is found that they occur ca. 100 mV more positive in the complexes. Thus, curiously, although ruthenium pentammine groups are typical electron donor groups, they have a small favorable effect on the ligand reduction potential. This is probably due to the influence of the 2+ charge of the terminal groups.

Mixed-Valence Ruthenium(II)–Ruthenium(III) Complexes and Intervalence Transitions. Since the comproportionation constant appears to be very close to the statistical limit, there is no way to prepare the pure mixed-valence species in solution (The situation can be different in the solid state, where interaction with the anions could modify the balance between the mixed-valence state and the mixture of homovalent states.) In the present study, which is performed in solution, all information on these compounds comes from the observation of the intervalence band in the near-IR region.

We first performed titration experiments on the complex $\mathbf{2}_{Ru}$ in D_2O containing 0.1 M DCl to avoid disproportionation of the ruthenium(III) species. During the oxidation, the evolution of the visible spectrum is continuous, with a decrease of the metal-to-ligand charge-transfer band (see Figure 4) and a modification in the position of the $\pi\pi^*$ band of the ligand. A new band appears, near 440 nm for the fully oxidized species. As in the case of the binuclear complex bridged by dipyridylethylene,[15] it is probably a ligand-to-metal charge transfer. In principle, this assignment could be secured by the study of the solvent influence, since it has been shown that, in pentaammineruthenium complexes, the ligand-to-metal charge-transfer bands move to higher energies when the *donor number* of the solvent increases, while the reverse is true for metal-to-ligand charge transfers.[30] In the present case, solubility problems limited us to the use of a few solvents; however, in dimethylformamide, a strong donor solvent, the band was observed as a shoulder near 425 nm, in qualitative agreement with the above interpretation.

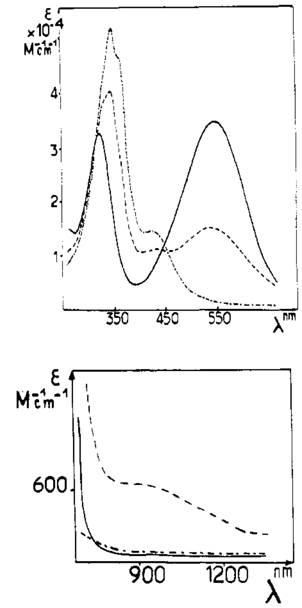

Figure 4. Ultraviolet–visible spectra (top) and near-infrared spectra (bottom) of the binuclear comples $\mathbf{2}_{Ru}$ during progressive oxidation by bromine in D_2O containing 0.1 M DCl (extinction coefficients refer to the total concentration of dimer): (—) initial spectrum; (---) half-oxidized species; (-·-) fully oxidized species.

During the oxidation, a band develops near 900 nm as a shoulder on the tail of the intense charge-transfer transition. It rises to a maximum, which is reached when 1 equiv of oxidant has been added, and then decreases. This sequence of spectral changes could be reversed by adding Eu^{2+} as reducing agent. These observations coupled with data on similar systems[14,31] allow us to assign this near-IR band to the intervalence transition. The apparent extinction coefficient was 630 M^{-1} cm^{-1}, which corresponds to a true value of 1260 M^{-1} cm^{-1} when the comproportionation equilibrium is taken into account.

The same experiment performed with the longer systems gave only disappointing results, the intervalence band appearing more and more buried in the tail of the charge-transfer transition. This is a consequence of the Marcus–Hush equation,[32] giving the contribution of the solvent to the intervalence transition energy

$$E_{out} = \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right)\left(\frac{1}{2a_A} + \frac{1}{2a_B} - \frac{1}{R}\right) \qquad (1)$$

where ϵ_s and ϵ_{op} are the static and optical dielectric constants (the latter taken as the square of the index of refraction), a_A and a_B are the radii of the coordination spheres of the two redox sites, R is the metal–metal separation, and the other symbols have their usual meanings. Thus, the longer the bridge, the higher the energy of the intervalence transition.

In order to achieve a better resolution of the intervalence transition, several solvents have been tried. According to the Marcus–Hush equation the best solvents correspond to low values of the $1/\epsilon_{op} - 1/\epsilon_s$ parameter. At the same time, it is necessary to shift the metal-to-ligand charge-transfer transition in the opposite direction, which is possible because it fortunately depends upon an independent solvent parameter, the donor number, as mentioned above. Thus, one has to look for a solvent with a *low donor number*.[30] Finally, we have chosen nitrobenzene; it is then impossible to use bromine as oxidant, since Br^- gives rise to strong ion pairs in this medium and considerably shifts the intervalence

---

(27) Woitellier, S.; Launay, J. P.; Joachim, C. To be submitted for publication.

(28) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

(29) Most values of K_c reported in the literature have been obtained in water, whereas our oxidation experiments have been performed in nitrobenzene. However, K_c does not seem to depend very much on the nature of the solvent.[15]

(30) Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 224.

(31) Stein, C. A.; Lewis, N. A.; Seitz, G. *J. Am. Chem. Soc.* **1982**, *104*, 2596.

(32) Cannon, R. D. *Electron Transfer Reactions*; Butterworths: London, 1980; p 188.

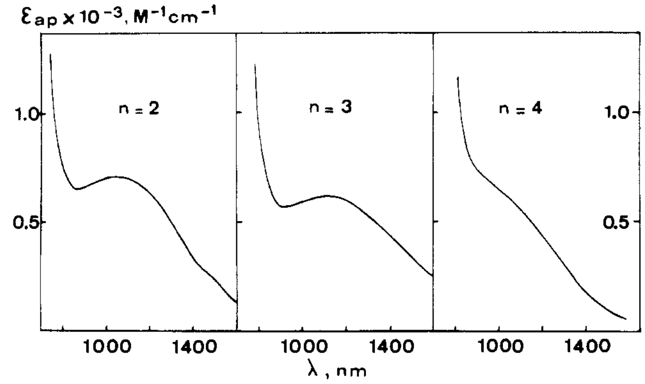

Figure 5. Intervalence bands for the mixed-valence complexes derived from $\mathbf{2}_{\mathrm{Ru}}$, $\mathbf{3}_{\mathrm{Ru}}$, and $\mathbf{4}_{\mathrm{Ru}}$. Extinction coefficients are apparent values calculated with respect to the total concentrations of dimers. The solvent is nitrobenzene.

transition. Thus, by the method of Curtis et al.,[21] the oxidation has been performed with $[Fe(bpy)_3](PF_6)_3$. A comparison of Figures 4 and 5 shows the improved resolution of the intervalence band under these conditions.

The compounds $\mathbf{3}_{\mathrm{Ru}}$ and $\mathbf{4}_{\mathrm{Ru}}$ have been studied by this procedure, and the near-IR spectra are gathered in Figure 5. Curiously, as one goes from $n = 2$ to $n = 3$, there is a small shift toward *lower energies* (see Table IV), contrary to the prediction of the Marcus–Hush equation. For $n = 4$, the shift seems to be toward higher energies, since the band appears only as a shoulder (see Figure 5). These nonmonotonous variations could be due to specific solvation effects, since the solvent molecules are particularly large and polarizable and the approximation of the dielectric continuum is certainly not completely valid.

Electronic Interaction in the Mixed-Valence Species. The main result emerging from a comparison of the spectra displayed in Figure 5 is that there is practically no variation in the intervalence band intensity with changes in n. If we take into account the fact that true extinction coefficients have been calculated by assuming $K_c = 4$, which is not strictly valid for the shorter systems, we probably have in fact a small increase in the band intensity with n.

The intensity of the intervalence transition is proportional to the square of the transition dipole moment, which is itself related to the degree of mixing of the zero-order wave functions by the equation[33]

$$M = e\alpha R \qquad (2)$$

where α is the degree of mixing and R is the metal–metal distance.

This enables an evaluation of the effective electronic coupling parameter V_{ab} between the two metal sites, by the relation

$$\alpha = V_{ab}/E_{IVT} \qquad (3)$$

where E_{IVT} is the energy of the intervalence transition, giving finally

$$M = eRV_{ab}/E_{IVT} \qquad (4)$$

For practical applications, the following equation is used:[6a,7,34,35]

$$V_{ab}\,(\mathrm{cm}^{-1}) = \frac{2.06 \times 10^{-2}}{R}(\epsilon_{max}\bar{\nu}_{max}\Delta\bar{\nu}_{1/2})^{1/2} \qquad (5)$$

in which R is in Å, ϵ_{max} is the extinction coefficient, and $\bar{\nu}_{max}$ is the transition energy and $\Delta\bar{\nu}_{1/2}$ the full width at half-maximum (both in cm^{-1}).

Table IV. Intervalence Band Parameters[a] and Derived Electronic Coupling Parameters for the Mixed-Valence Complexes

parent complex	$\bar{\nu}_{max}$, cm^{-1} [b]	$\Delta\bar{\nu}_{1/2}$, cm^{-1} [c]	ϵ, $M^{-1}\,cm^{-1}$ [d]	R, Å [e]	V_{ab}, cm^{-1} [f]
$\mathbf{2}_{\mathrm{Ru}}$	9615	4900	1430	15.8	340
$\mathbf{3}_{\mathrm{Ru}}$	9010	4700	1250	18.1	260
$\mathbf{4}_{\mathrm{Ru}}$	~10000[g]	~4800	~1220[g]	20.6	~240

[a] In nitrobenzene. [b] Band position. [c] Full width at half-maximum. [d] Assuming $K_c = 4$. [e] Metal–metal distance, from molecular models. [f] From eq 5. [g] Shoulder.

The results of the calculations are shown in Table IV. $\Delta\bar{\nu}_{1/2}$ has been taken as twice the half-width determined in the right part of the spectrum. In the case of $n = 4$, this procedure certainly overestimates the intervalence band intensity, due to the mixing with the charge-transfer transition. Thus, the reported values for ϵ_{max} and V_{ab} can be considered as upper limits. With the raw values of Table IV, it is found that V_{ab} decreases by about 30% when going from $n = 2$ to $n = 4$. The true decrease should be higher if we take into account the difficulty with $n = 4$, but as mentioned above, the influence of K_c in the measurement process has an opposite effect, because in the short systems K_c is probably greater than 4. Anyway, this rate of decrease of V_{ab} is rather modest and is corroborated by extended Hückel calculations.[27] Thus, the electronic interaction is transmitted well by the conjugated backbone, at least much better than the transmission across saturated systems like proteins.[1]

The very slow decrease of the electronic interaction with increase in n has been predicted by Larsson,[5] using molecular orbital calculations, the electronic coupling being deduced from an orbital splitting. More recently, Joachim[9] has reached a similar conclusion using effective Hamiltonian theory to extract coupling parameters in a systematic way from quantum-mechanical calculations. However, to our knowledge, this is the first time that these predictions have been experimentally tested in a homologous series of compounds. This shows the possibility to connect distant redox or active sites by some kind of "molecular wiring".

We are presently extending the systems of the present class to investigate longer bridges and different metals. The effect of isomerization of the bridging ligand is also under investigation.

Acknowledgment. Thanks are due to S. Hunig for advice on the synthesis of dipyridylbutadiene and the gift of a sample of convenient glyoxal. The financial support of Roussel-Uclaf is also gratefully acknowledged.

Registry No. **2**, 118494-72-7; $\mathbf{2}_{\mathrm{Ru}}(PF_6)_4$, 118494-75-0; $\mathbf{2}_{\mathrm{Ru}}{}^{5+}$, 106219-83-4; $\mathbf{2}_{\mathrm{Ru}}{}^{6+}$, 118494-80-7; **3**, 118464-76-9; $\mathbf{3}_{\mathrm{Ru}}(PF_6)_4$, 118494-77-2; $\mathbf{3}_{\mathrm{Ru}}{}^{5+}$, 118494-83-0; $\mathbf{3}_{\mathrm{Ru}}{}^{6+}$, 118494-81-8; **4**, 118513-63-6; $\mathbf{4}_{\mathrm{Ru}}(PF_6)_4$, 118494-79-4; $\mathbf{4}_{\mathrm{Ru}}{}^{5+}$, 118494-84-1; $\mathbf{4}_{\mathrm{Ru}}{}^{6+}$, 118494-82-9; $(C_2H_2O_2)_3{\cdot}H_2O$, 4405-13-4; $[Ru(NH_3)_2Cl]Cl_2$, 18532-87-1; $[(NH_3)_5Ru(H_2O)](PF_6)_2$, 34843-18-0; Br_2, 7726-95-6; $[Fe(bpy)_3](PF_6)_3$, 28190-88-7; 4-pyridylcarbinol, 586-95-8; (bromomethyl)-4-pyridinium bromide, 73870-24-3; triphenyl(4-picolyl)phosphonium bromide, 73870-23-2; tetraethyl ((*E*)-2-butene-1,4-diyl)diphosphonate, 16626-80-5; pyridine-4-carboxaldehyde, 872-85-5; tetraethyl ((*E*),(*E*)-2,4-hexadiene-1,6-diyl)diphosphonate, 118494-73-8.

---

(33) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

(34) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(35) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.