separated with a silica gel column. When the number of the IrCp* groups, n, is increased, the solubility of these clusters in water is decreased. The ^1H NMR spectrum of $[(RhCp^*)_{4-n}$-$(IrCp^*)_nV_6O_{19}]$ ($0 \leq n \leq 4$) displays two resonances having relative intensities of $(4 - n):n$ in the methyl region of the Cp* group, and the methyl signals of the IrCp* groups always appear at a higher field than that of the RhCp* groups. The chemical shift values of both methyl groups decrease with increasing number of n in $[(RhCp^*)_{4-n}(IrCp^*)_nV_6O_{19}]$. In the ^{13}C NMR spectra, two sets of the methyl and the ring carbon signals were observed at δ ca. 9.4 and 94.5 (d, $J_{Rh-C} = 8.9$ Hz) for RhCp* and δ ca. 9.9 and 87.0 for IrCp*, respectively. Figure 7 shows the ^{51}V NMR spectrum of clusters 1–5 in CD_2Cl_2. The ^{51}V NMR spectra of these substituted clusters show the difference in the chemical environment of the vanadium atoms clearly. When one IrCp* group is substituted for a RhCp* group, the resulting $[(RhCp^*)_3(IrCp^*)V_6O_{19}]$ has two equally intense signals. When two or three RhCp* groups are replaced, three or two signals are observed. These chemical environments around the vanadium atom of the substituted clusters are shown in Figure 8. The chemical environments are classified into three types: the first has two adjacent rhodium atoms (δ −511 to −512; filled circle in Figure 8), the second has one adjacent rhodium and iridium atoms (δ −517 to −518; dashed circle in Figure 8), and the third has two adjacent iridium atoms (δ −527 to −529; open circle in Figure 8). The intensity ratios of these signals are proportional to the number of vanadium atoms. The assignments were easily made by comparison of the NMR data of the substituted clusters, since the vanadium at the rhodium–coordinated site is more deshielded than that of the iridium-coordinated site. The line widths of the iridium-substituted clusters were found to be wider by 35–114 Hz than that of cluster 1.

Conclusions. We have synthesized the organometallic oxide cluster $[(MCp^*)_4V_6O_{19}]$ (1 and 2) using VO_3^- and $[MCp^*Cl_2]_2$ as a model compound for the inorganic oxide-bound RhCp* groups, which is much more active and selective for hydroformylation.[15,16] The new quadruple-cubane framework, which contains a structure similar to the fragment structure of V_2O_5, has a more well-balanced structure in the solid state than the other hexametalates. This cluster has a fixed framework in organic

solvents and a remarkable amphiphilic character in spite of being a neutral molecule with a quite large molecular weight. The discrete $V_6O_{19}{}^{8-}$ has not yet been prepared and is thought to be quite labile in solution,[29] but other $M_6O_{19}{}^{n-}$ types ($n = 8$, Nb, Ta; $n = 2$, Mo, W) have been isolated as some of the most stable polyoxoanions. This fact seems to be attributed to the smaller radii of V^{5+} (0.68 Å in coordination number (CN) 6), which interferes with the assembly of a cagelike structure with the VO_6 unit, compared with other metals in the same CN 6 (Nb^{5+}, 0.78 Å; Ta^{5+}, 0.78 Å; Mo^{6+}, 0.73 Å; W^{6+}, 0.74 Å).[47] The RhCp* groups balance the framework of the V_6O_{19} core by its symmetrical binding, and the Cp* groups sterically hinder attack of the solvent molecules in nonaqueous solvents. The exchange reaction of oxygen proceeds selectively at the bridging oxygen on heating in neutral aqueous solution, and the dissociation reaction of the organometallic groups takes place in acidic aqueous solution. The substitution reaction of the organometallic groups was performed by the introduction of other organometallic groups to an acidic solution of cluster 1. That is a useful method to construct the cluster framework in a rational synthesis. In the case of the mixed cluster with the unavoidable disorder problems, the combination of X-ray crystallography and multinuclear NMR spectroscopy gives a good probe for revealing the structures of the mixed clusters.

Supplementary Material Available: A table of crystallographic data, an ORTEP diagram of cluster 3, and tables of anisotropic temperature factors (4 pages); listings of observed and calculated structure factor amplitudes (30 pages). Ordering information is given on any current masthead page.

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Control of Intramolecular Electron Transfer by a Chemical Reaction. The 4,4'-Azopyridine/1,2-Bis(4-pyridyl)hydrazine System

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The complexation of 4,4'-azopyridine by the pentaammineruthenium(II) group is described. The metal sites are coordinated to the pyridyl nitrogen atoms and interact through the conjugated azo linkage. Upon oxidation, an intervalence absorption is detected, but it is unresolved with respect to the nearby metal-to-ligand charge-transfer band. The acidification of the binuclear pentaammineruthenium(II) complex gives rise to a pH induced intramolecular redox reaction yielding a ruthenium(III) complex of the reduced form of 4,4'-azopyridine, i.e. 1,2-bis(4-pyridyl)hydrazine. Reduction of the latter complex allows the investigation of intervalence transfer through 1,2-bis(4-pyridyl)hydrazine. It is found that the electronic interaction is greatly reduced in the reduced form of the ligand with respect to the oxidized form. This modification is discussed in the frame of an extended Huckel molecular orbital calculation.

Introduction

Intramolecular electron transfer is one of the basic processes involved in molecular electronics. Thus long molecules containing two redox sites linked by a conjugated pathway can be considered as "molecular wires".[1,2] To go further, it is necessary to devise

molecules in which the electronic coupling could be modified by an external perturbation, thus playing the role of switches. A first possibility would be to change the geometry by a photophysical excitation, and such compounds are currently under investigation.[3]

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Another possibility is to make use of some chemical reaction that would alter the degree of conjugation in the link connecting the two redox sites.[4]

One of the simplest chemical reaction being protonation, we have thought that the introduction of nitrogen atoms in the conjugated link could be a way to introduce a chemical reactivity. Among the different functional groups containing nitrogen, the azo group offers several specific advantages: good chemical stability; good efficiency to transmit electronic effects;[5] sensitivity of the electronic structure upon certain parameters such as acidity;[6] possibility of cis–trans isomerization.[7] We have thus studied the properties of 4,4′-azopyridine (abbreviated azpy) as a bridging ligand in binuclear bis(pentaammineruthenium) complexes, and particularly the properties of the mixed-valence diruthenium-(II/III) complex. The behavior of the system upon protonation has been investigated, and it has been shown that an intramolecular redox reaction occurs. Thus the 4,4′-azopyridine ligand is transformed into the reduced form 1,2-bis(4-pyridyl)hydrazine (abbreviated bphy). This has a strong influence on the through bond metal–metal electronic coupling. A preliminary report has already appeared.[8]

Experimental Section

UV–visible–near-IR spectra were recorded with a Beckman 5240 or a Shimadzu UV-3100 spectrophotometer. Cyclic voltammetry was performed with Tacussel equipment, usually in dimethylformamide containing 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte. The working electrode was a platinum wire and the reference electrode an aqueous saturated calomel electrode equipped with a double-frit system. Some experiments have also been performed on mercury electrodes (hanging mercury drop electrode or dropping mercury electrode). Resonance Raman spectra were performed in acetonitrile, with an excitation at 514 or 647 nm.

The synthesis of air-sensitive compounds, in particular the ruthenium complexes, were performed in Schlenk tubes, under an argon atmosphere.

4,4′-Azopyridine (azpy). 4,4′-Azopyridine was prepared by oxidative coupling of 4-aminopyridine by hypochlorite, using an adaptation of published procedures.[7,9] A 100-mL aliquot of a cold solution of 4-aminopyridine (5 g) in water was added dropwise to 300 mL of a 10% NaOCl solution. The mixture was stirred at 0 °C as an orange precipitate formed. Filtration was performed a few minutes after the end of addition, and the aqueous phase and the precipitate were extracted with diethyl ether. The ether phases were gathered, dried on MgSO₄, and evaporated. The crude product was purified by chromatography on Al₂O₃ (eluent: acetone/hexane 1/10). Recrystallization in water yielded 4,4′-azopyridine as long orange needles, mp 107–108 °C (lit. mp 107.5–108 °C). Yield: 3.8 g (20 mmol, 77%).

Anal. Calcd for $C_{10}H_8N_4$: C, 65.22; H, 4.35; N. 30.43. Found: C, 65.05; H, 4.15; N, 30.17.

UV–vis in heptane (λ_{max}, nm (molar decadic absorption coefficient in mol⁻¹ L cm⁻¹)): 460 (235), 286 (17 300).

[(NH₃)₅Ru–azpy](PF₆)₂. The mononuclear pentaammineruthenium-(II) complex was prepared by reaction between 4,4′-azopyridine and [(NH₃)₅Ru(H₂O)](PF₆)₂·H₂O prepared as described.[2,10]

The ruthenium precursor complex (0.512 g, 1 mmol) was dissolved in 20 mL of deaerated acetone in a Schlenk tube, while 0.736 g of ligand (4 mmol) was dissolved in 20 mL of acetone, in another Schlenk tube. Then the Ru(II) solution was transferred into the flask containing the ligand with a cannula. The transfer was made over 5 min in order to minimize the formation of binuclear species. After being stirred for 2 h at room temperature, the solution was treated with 200 mL of dry deaerated diethyl ether and the blue precipitate that formed was col-

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Table I. UV–Visible Spectral Data[a] for the Mononuclear and Binuclear Complexes with 4,4′-Azopyridine and for the Binuclear 1,2-Bis(4-pyridyl)ethylene Complex[14]

compound	solvent	ππ*	MLCT
[(NH₃)₅Ru–azpy]²⁺	water	276 (12 500)	668 (10 500)
	acetonitrile	283 (13 500)	645 (11 500)
[(NH₃)₅Ru–azpy–Ru(NH₃)₅]⁴⁺	water	287 (10 000)	721 (11 500)
	acetonitrile	287 (10 000)	710 (12 000)
	dmf	290 (9000)	833 (14 500)
[(NH₃)₅Ru–bpe–Ru(NH₃)₅]⁴⁺	water	294 (19 000)	545 (28 200)

[a] Wavelengths in nanometers; molar extinction coefficients in parentheses.

lected, washed with diethyl ether, and dried in vacuo. Yield: 0.525 g (0.80 mmol, 80%).

Anal. Calcd for $C_{10}H_{23}N_9RuP_2F_{12}$: C, 18.18; H, 3.48; N, 19.09. Found: C, 18.44; H, 3.62; N, 18.25.

[(NH₃)₅Ru–azpy–Ru(NH₃)₅](PF₆)₄. The binuclear pentaammine-ruthenium(II) complex was prepared by a similar procedure using 1.024 g (2 mmol) of the ruthenium precursor complex [(NH₃)₅Ru(H₂O)](P-F₆)₂·H₂O in 40 mL of acetone under argon and 0.184 g of ligand (1 mmol) in 10 mL of acetone. The ruthenium solution was then transferred into the ligand solution with a cannula. After being stirred for 2 h at room temperature, the solution was treated with 200 mL of dry, deaerated diethyl ether and the blue precipitate was collected and dried in vacuo. Yield: 1.08 g (0.95 mmol, 95%).

Anal. Calcd for $C_{10}H_{38}N_{14}Ru_2P_4F_{24}$: C, 10.56; H, 3.35; N, 17.25; Ru, 17.78. Found: C, 10.01; H, 3.67; N, 16.53; Ru, 16.50.

[(NH₃)₅Ru–azbz](PF₆)₂ (azbz = Azobenzene). This complex was prepared by the same procedure as the 4,4′-azopyridine complex by using 1.024 g (2 mmol) of [(NH₃)₅Ru(H₂O)](PF₆)₂·H₂O and 1.092 g (6 mmol) of azobenzene. After 2 h the product was precipitated by diethyl ether, filtered, and washed with diethyl ether, giving a green product. Yield: 0.92 g (1.4 mmol, 70%).

Anal. Calcd for $C_{12}H_{25}N_7RuP_2F_{12}$: C, 21.88; H, 3.80; N, 14.89; P, 9.42. Found: C, 19.83; H, 3.84; N, 15.11; P, 7.12.

1,2-Bis(4-pyridyl)hydrazine (bphy). A 0.46-g sample of 4,4′-azopyridine (2.5 mmol) was dissolved in 50 mL of deaerated ethanol and mixed with 0.6 g of granulated Zn and 20 mL of concentrated ammonia. The mixture was stirred for 30 min at 80 °C under argon, during which discoloration occurred. It was then filtered under argon, using Schlenk tubes and cannula, to eliminate excess zinc and zinc hydroxyde. After concentration in vacuo, 100 mL of deaerated water was added, yielding a white precipitate. It was filtered under argon, washed with ether, and dried in vacuo. A second crop could be obtained by vacuum evaporation at 50–60 °C of the filtrate. The total yield was 68%.

Anal. Calcd for $C_{10}H_{10}N_4·^1/_3H_2O$: C, 62.50; H, 5.55; N, 29.16. Found: C, 62.44; H, 5.15; N, 28.94.

UV in water: 274 nm (24 500), 250 (sh) nm.

[(NH₃)₅Ru–bphy–Ru(NH₃)₅](PF₆)₄. The procedure was the same as for the 4,4′-azopyridine complex although it was complicated by the low solubility of hydrazobis(pyridine) in all solvents. Thus 0.93 g (5 mmol) of 1,2-bis(4-pyridyl)hydrazine was suspended in 50 mL of acetone, and solid [(NH₃)₅Ru(H₂O)](PF₆)₂·H₂O (5.12 g, 10 mmol) was directly added. The mixture was stirred for 4 h at room temperature in the dark and then precipitated with 400 mL of diethyl ether, yielding a yellow solid. [(NH₃)₅Ru–bphy–Ru(NH₃)₅](PF₆)₄ is very sensitive toward oxygen, and even with argon protection, it was not possible to use it for quantitative measurements. UV–vis in acetonitrile: 375, 245 nm.

Oxidation Experiments. Oxidations to generate the mixed-valence ruthenium(II)–ruthenium(III) species were performed in nitrobenzene or D₂O, using either Br₂ or [Fe(bpy)₃](PF₆)₃[11] as an oxidant. In some cases, a reduction was performed in aqueous solution, using Eu²⁺.[12]

Results and Discussion

4,4′-Azopyridine as a Bridging Ligand. Reaction of the 4,4′-azopyridine ligand with [(NH₃)₅Ru(H₂O)]²⁺ in acetone yields the deep blue mononuclear and binuclear complexes. Their electronic spectra are shown in Table I, together with the spectrum of the binuclear 1,2-bis(4-pyridyl)ethylene complex.

The azopyridine ligand has four possible sites of coordination, namely the two pyridine nitrogens and the two azo nitrogens. The former are much more accessible for coordination for sterical reasons, and for the binuclear complex, the two pentaammine ruthenium groups are assumed to be fixed there. Additional

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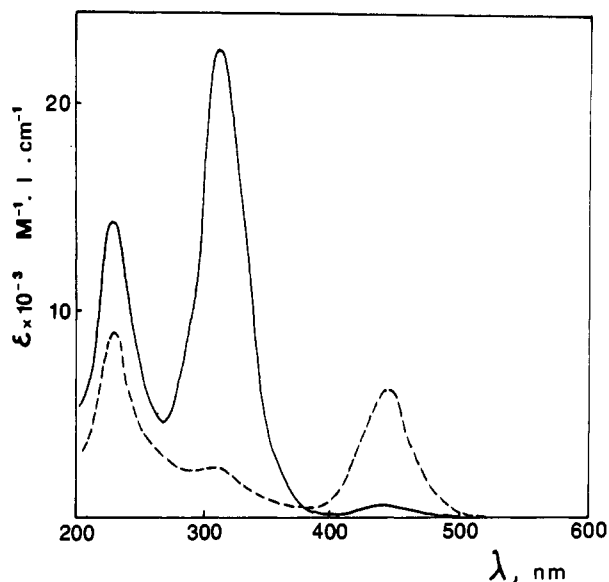
Figure 1. UV–visible spectra of free 4,4'-azobenzene (solid curve) and of the $[(NH_3)_5Ru-azbz]^{2+}$ complex (dotted curve) in acetonitrile.

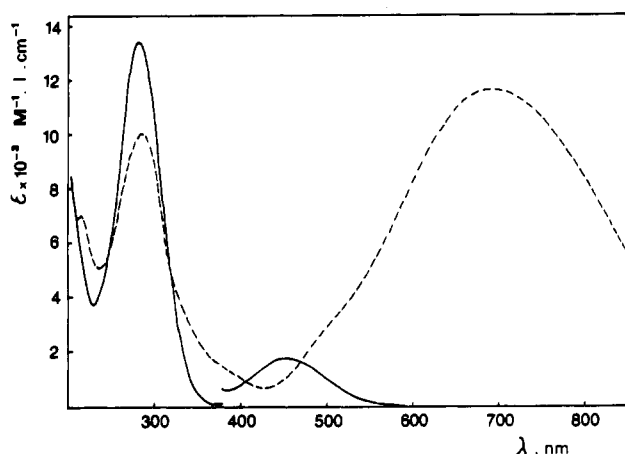**Figure 2.** UV–visible spectra of free 4,4'-azopyridine (solid curve) and of the $[(NH_3)_5Ru-azpy-Ru(NH_3)_5]^{4+}$ complex (dotted curve) in aceto-nitrile. The spectrum of free 4,4'-azopyridine is magnified 10 times between 380 and 600 nm to show the n–π^* band.

observations rule out a coordination on the azo group: (i) The N=N Raman band is still observed by resonance Raman spectroscopy at 1454 cm^{-1} in $[(NH_3)_5Ru-azpy-Ru(NH_3)_5]^{4+}$, instead of 1466 cm^{-1} in the free ligand.[13] This shift can be assigned to a weakening of the N=N bond due to the donor character of the pentaammineruthenium groups, thus populating the LUMO of the ligand, which is antibonding between the two nitrogens. A much larger shift would be anticipated for a coordination on the azo group. (ii) We have prepared the azobenzene complex where coordination necessarily occurs on the azo group. It is then found that complexation strongly modifies the electronic spectrum of the ligand (Figure 1). By contrast, in $[(NH_3)_5Ru-azpy-Ru(NH_3)_5]^{4+}$, the ligand UV bands are observed near their usual position (Figure 2).

For both the mononuclear and the binuclear azopyridine complex, two intense bands are observed, one in the ultraviolet between 270 and 290 nm, corresponding to the $\pi \rightarrow \pi^*$ transition of the ligand, and one in the visible, between 650 and 830 nm. Comparison with the case of the isoelectronic 1,2-bis(4-pyridyl)ethylene ligand[14] and with other systems of the same class[15] shows that this band corresponds to a metal-to-ligand charge transfer
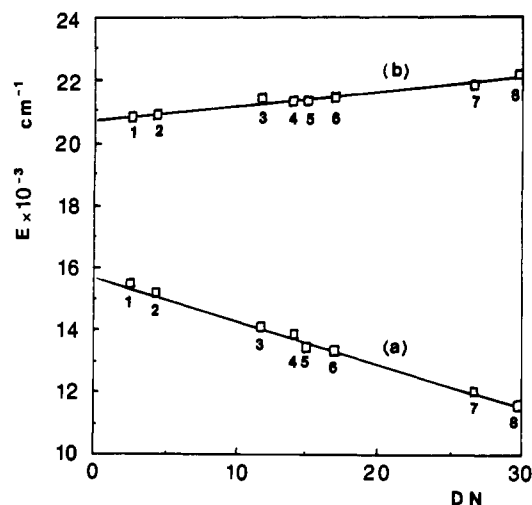

Figure 3. Solvatochromic plot for the visible band energy versus the donor number of the solvent: (a) blue form of the binuclear complex, i.e. $[(NH_3)_5Ru-azpy-Ru(NH_3)_5]^{4+}$; (b) red form of the binuclear complex obtained in acidic medium. Key for solvents: 1 = nitromethane, 2 = nitrobenzene, 3 = benzonitrile, 4 = acetonitrile, 5 = propylene carbonate, 6 = acetone, 7 = dmf, and 8 = dmso.

Table II. Electrochemical Results[a] in DMF on a Platinum Wire Electrode

compound	peak positions, V vs SCE		
	anodic	cathodic	
azpy		–0.79 (rev)	–1.54 (irrev)
$[(NH_3)_5Ru-azpy]^{2+}$	+0.18 (rev)	–0.74 (rev)	–1.11 (irrev)
$[(NH_3)_5Ru-azpy-Ru(NH_3)_5]^{4+}$	+0.20 (rev)	–0.77 (rev)	–1.26 (irrev)

[a] rev = reversible peak; irrev = irreversible peak.

(MLCT). In particular, the characteristic solvent dependence for this type of transition is observed, the band moving to lower energies when the donor number of the solvent increases[16] (see Figure 3a for the binuclear complex and Table I).

When the binuclear complexes of azopyridine and 1,2-bis(4-pyridyl)ethylene are compared, it is found that the MLCT band is at a lower energy and exhibits a *weaker* extinction coefficient in the former (Table I). These effects can be rationalized by taking into account the perturbations introduced by the replacement of the central CH groups of 1,2-bis(4-pyridyl)ethylene by the more electronegative nitrogen atoms. This lowers the ligand LUMO energy and thus decreases the energy of the charge transfer transition. In agreement with this, it can be noticed that 4,4'-azopyridine is a particularly easily reducible ligand. The free ligand is reduced at –0.79 V in DMF[17] whereas 1,2-bis(4-pyridyl)ethylene is reduced at –1.61 V.[18]

The change in intensity of the charge transfer when going from 4,4'-azopyridine to 1,2-bis(4-pyridyl)ethylene is at first sight surprising, because the lowering of the ligand LUMO should increase the mixture with ruthenium orbitals. But, at the same time, it changes the coefficients of the LUMO on the terminal nitrogen atoms by draining some electron density on the central nitrogen atoms. According to Ernst and Kaim[19] there is a correlation between the LUMO coefficient on the terminal nitrogen atom of the free ligand and the intensity of the charge-transfer band of the complex, higher coefficients giving higher intensities. Our extended Huckel calculations show that this coefficient varies from 0.352 in 1,2-bis(4-pyridyl)ethylene to 0.260 for 4,4'-azopyridine, which is enough to explain the change in intensity (ϵ

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= 28 200 for the 1,2-bis(4-pyridyl)ethylene complex in water,[14] vs 11 500 for the 4,4'-azopyridine complex).

Cyclic voltammetry of $[(NH_3)_5Ru-azpy]^{2+}$ and $[(NH_3)_5Ru-azpy-Ru(NH_3)_5]^{4+}$ in DMF on a platinum electrode shows in the cathodic part the characteristic features of the ligand (see Table II). An anodic peak is observed near +0.2 V (reversible) corresponding to the ruthenium(II/III) couple. For the binuclear complex, no sign of splitting in two monoelectronic waves was observed on platinum. With mercury electrodes, a small bump could be observed on the rising part of the anodic peak, which could correspond to the beginning of a splitting. The comproportionation constant defined as

$$K_c = (II-III)^2/(II-II)(III-III)$$

could not be reliably determined by electrochemical methods, but it is determined below by equilibrium titration.

Intervalence Transition in $[(NH_3)_5Ru-azpy-Ru(NH_3)_5]^{5+}$. Oxidation of the mono and binuclear complexes could be easily performed by bromine in water. In both cases, there was a continuous decrease of the MLCT band intensity, which disappeared for 1 equiv/mol of ruthenium.

Oxidation of the binuclear ruthenium(II) dimer (abbreviated as II-II) was studied in order to obtain the mixed valence ruthenium(II)-ruthenium(III) species (II-III). Owing to the comproportionation equilibrium, the actual proportion of mixed-valence species defined as $P = (II-III)/[(II-II) + (III-III) + (II-III)]$ never reaches 1. When half of the total ruthenium has been oxidized to the 3+ state, P reaches its maximum value given by

$$P = K_c^{1/2}/(2 + K_c^{1/2})$$

The mixed-valence species (II-III) can be qualitatively characterized in all cases because it displays an intervalence transition that is absent in the spectra of the homovalent species. The comproportionation constant was determined by redox titration under argon. The detection of the intervalence band was complicated by the unusually low energy of the metal-to-ligand charge transfer, the tail of which extends in the near-infrared region where the intervalence band is expected. Two solvents were used: (i) D_2O because it has a large spectral window (200–1850 nm) and it allows accurate solution studies with K_c determination and (ii) nitrobenzene because it shifts the intervalence band to the red and the charge-transfer band to the blue[16,20] so that a better resolution can be expected. On the other hand, a quantitative study in nitrobenzene is much more difficult and was not undertaken due to the difficulty of adding known aliquots of oxidant and to the possible effects of ion pairing.

In D_2O, we first performed an oxidation of a 10^{-4} M solution of the binuclear complex by 10^{-2} M bromine in 1-cm cells. Upon addition of the oxidant, the optical density of the MLCT band decreased continuously, without modification of the wavelength maximum. Using then a more concentrated solution (7×10^{-4} in binuclear complex), we found that in the near-IR region, between 1100 and 1860 nm, the optical density *passed through a maximum*. This phenomenon was completely reversible, and under dioxygen-free conditions we obtained the same spectra by reduction of the (III-III) to the (II-II) species with Eu^{2+}. This behavior is typical of an intervalence absorption. However no distinct intervalence band really separated from the charge-transfer band could be observed.

It is nevertheless possible, from the results of titration, to determine the value of the comproportionation constant.[12] The optical density at a fixed wavelength (here 1600 nm) was recorded as a function of the amount of oxidant. From this curve, we found $K_c = 40 \pm 5$ for the binuclear $[(NH_3)_5Ru-azpy-Ru(NH_3)_5]^{4+}$ complex. This value is appreciably higher than in the isoelectronic 1,2-bis(4-pyridyl)ethylene complex,[14] for which $K_c = 14$. This result is in agreement with the conclusion of Sutton and Taube[14] that the main contribution to the thermodynamic stability of these
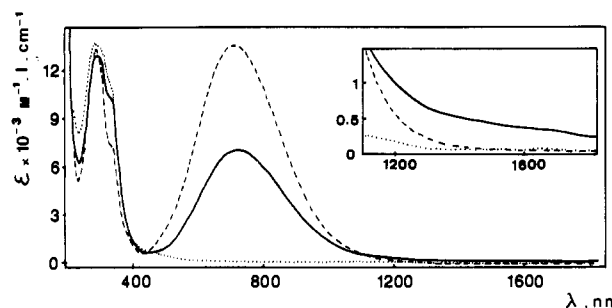
(20) Hupp, J. T.; Meyer, T. J. *J. Phys. Chem.* **1987**, *91*, 1001.

Figure 4. Spectra in D_2O for the $[(NH_3)_5Ru-azpy-Ru(NH_3)_5]^{n+}$ species: (- - -) II-II; (—) II-III (corrected from K_c); (···) III-III.
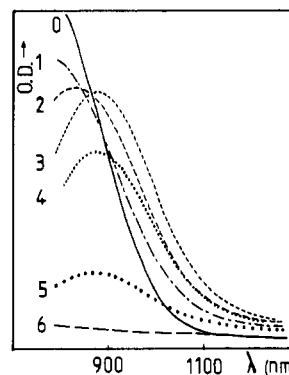

Figure 5. Titration of $[(NH_3)_5Ru-azpy-Ru(NH_3)_5]^{4+}$ (7×10^{-5} M in nitrobenzene) by bromine (10^{-3} M in nitrobenzene). The numbers on the curves are arbitrary, but correspond to increasing amounts of the oxidizing agent. Note that the optical density increases and then decreases in the 900–1300-nm range.

mixed valence compounds comes from the "synergetic effect". Coordinating a ruthenium(III) on one side of the ligand decreases the energy of the ligand LUMO and then strengthens the ruthenium(II) back-donation. In our case, this process would be strongly exalted by the intrinsic low energy of the ligand LUMO with respect to dipyridylethylene. Knowing the K_c value, it is then possible to compute the corrected spectrum of the mixed-valence species, which is displayed in Figure 4.

In nitrobenzene the oxidation yielded also a decrease of the metal-to-ligand charge-transfer band with the growing and decay of an absorption due to the mixed-valence species in the range 1100–1300 nm. Contrary to the case of water, there was a marked change in the position and shape of the visible band (Figure 5). We believe this is due to extensive mixing between the MLCT and intervalence bands.

We have tried several other different solvents and oxidizing agents, but no clear improvement with respect to the results presented here could be obtained. Thus, the best quantitative results come from D_2O measurements, and since there is no well-resolved intervalence band, we report for comparison purposes the corrected extinction coefficient at 1400 nm (this wavelength corresponding to the end of metal-to-ligand absorption). Taking into account the uncertainty on K_c, this corrected extinction coefficient is found between 490 and 510 M^{-1}/cm^{-1} (incidentally, it is fortunately not very sensitive to the K_c value introduced in the calculation). The corrected extinction coefficient appears small when compared to similar systems (cf. maximum extinction coefficients of 920 and 760 M^{-1} cm^{-1} for the dimers bridged by 4,4'-bipyridine and 1,2-bis(4-pyridyl)ethylene respectively[15]). But in the present system, the maximum of the band is certainly located below the metal-to-ligand charge-transfer band, and furthermore the intervalence band appears extremely broad. The intensity of the intervalence band is certainly much higher than suggested by a simple examination of its extinction coefficient at 1400 nm.

pH-Induced Intramolecular Redox Reaction. Addition of aqueous hydrochloric acid to an aqueous solution of the blue complex $[(NH_3)_5Ru-azpy-Ru(NH_3)_5]^{4+}$ (2.10^{-4} M, under argon) immediately generates a pink color. The reaction is rapid and

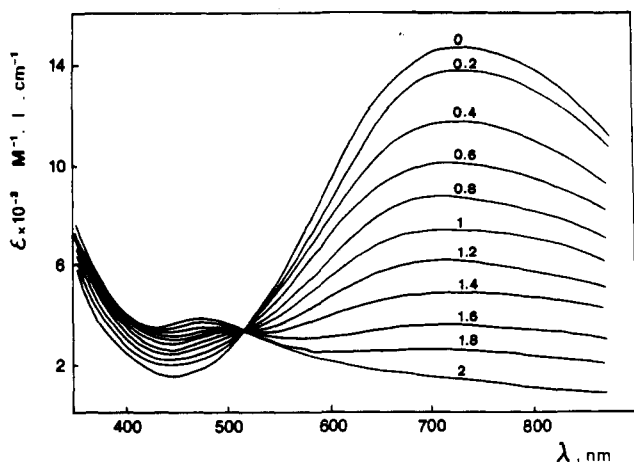**Figure 6.** Titration of $[(NH_3)_5Ru-azpy-Ru(NH_3)_5]^{4+}$ (3×10^{-4} M solution) by hydrochloric acid (10^{-2} M) in acetonitrile. The quantities of H^+ equivalent introduced per dimer unit are reported on each curve.

reversible. The intense MLCT disappears and a weaker band appears at 475 nm. An analogous reaction was observed with the mononuclear complex, but it is simpler to discuss the case of the binuclear complex first.

Spectrophotometric titration can be performed in acetonitrile showing that the reaction consumes two H^+ per mole (see Figure 6). In water the "pseudo pK" (i.e. the pH for which half-conversion has occurred) was found to be 4.6. However, these spectral changes cannot be explained by a simple protonation reaction of the central azo group, because in such a case a red shift should be observed. This is indeed what happens in the related system.[21]

λ_{max} = 460 nm


λ_{max} = 666 nm
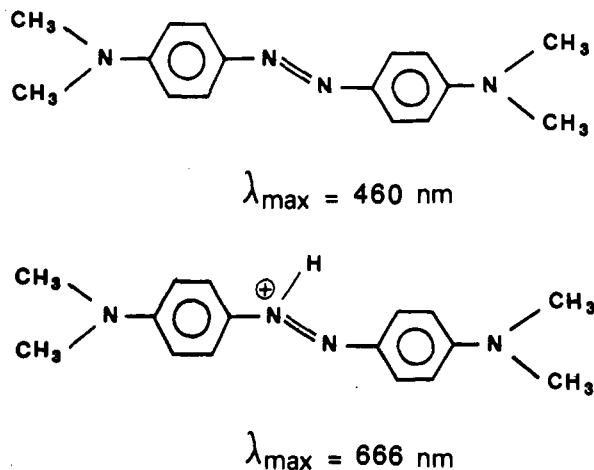
Additional observations are also inconsistent with a simple acid/base reaction. Thus the solvatochromic effect is now *reversed* with respect to the case of the starting product; i.e., a strongly donor solvent moves the band to the blue (Figure 3). Finally, the pink species exhibits a fairly intense and broad ESR signal in frozen solution. This suggests the presence of ruthenium(III), which is paramagnetic but gives broad signals as a result of orbital contribution.[22] The inverted solvatochromic effect is also a signature of ruthenium(III) because, in such a case, the observed transition corresponds to a ligand-to-metal charge transfer.[16] As strongly donor solvents stabilize the 3+ oxidation state (through H bonding with the ammonia hydrogens), they increase the energy of the transition corresponding to the intramolecular process

$$Ru^{III}-L \rightarrow Ru^{II}-L^{\bullet+}$$
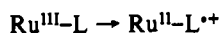
Finally, resonance Raman spectra of the pink form failed to show the characteristic N=N frequency.

All these observations suggest that the reaction induced by protons is

$$Ru^{II}py-N=N-py-Ru^{II} + 2\ H^+ \rightarrow$$
$$Ru^{III}-py-NH-NH-py-Ru^{III}$$
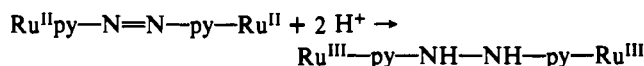
Such a reaction is not surprising if we consider the position of the redox potentials. Thus the 4,4'-azopyridine/1,2-bis(4-pyridyl)hydrazine couple is a reversible system in water, with E° near 0 V SCE at pH 7.[23] On the other hand, the $(NH_3)_5Ru^{2+/3+}$ system is observed near 0.2 V in the 4,4'-azopyridine complex. Thus the stable distribution of oxidation states is effectively Ru^{2+}-4,4'-azopyridine-Ru^{2+}. But since the 4,4'-azopyridine/1,2-bis(4-pyridyl)hydrazine couple involves protons, its apparent standard potential is expected to increase with acidity. Thus it not surprising that in acidic medium the distribution of oxidation states becomes Ru^{3+}-1,2-bis(4-pyridyl)hydrazine-Ru^{3+}. There is in addition a more subtle effect: when the ligand is in the form 1,2-bis(4-pyridyl)hydrazine, the $Ru^{2+/3+}$ couple is found near −0.07 V (see below). This provides a further stabilization for the Ru^{3+}-1,2-bis(4-pyridyl)hydrazine-Ru^{3+} configuration.

A confirmation of the above hypothesis would have been the isolation of the red form. But all attempts to isolate a pure solid sample have failed due to a partial conversion of the red form into the blue form during evaporation, which is ascribed to the effect of temperature. Thus to check the involvement of 1,2-bis(4-pyridyl)hydrazine in the above phenomena, we have independently prepared 1,2-bis(4-pyridyl)hydrazine by chemical reduction of 4,4'-azopyridine. The method was adapted from the reduction of azobenzene to 1,2-diphenylhydrazine.[17] This gives a white solid, very sparingly soluble in most solvents. It is extremely oxidizable when moist or in solution and regenerates orange 4,4'-azopyridine. The reaction with $[(NH_3)_5Ru(H_2O)](PF_6)_2 \cdot H_2O$ has been carried out as usual, using acetone as solvent. To avoid dilution, the ruthenium precursor was directly added to the acetone suspension as a solid. Although the main species thus obtained is certainly $[(NH_3)_5Ru-bphy-Ru(NH_3)_5](PF_6)_4$ it was found that the reaction is not quantitative. Purification proved impossible because the complex oxidizes very easily to give the deep blue 4,4'-azopyridine complex. Thus only qualitative characterizations can be given. The UV spectrum shows an intense band at 375 nm in acetone or acetonitrile, which we assign to the metal-to-ligand charge transfer. It is interesting to notice that the energy of this transition is higher than for the $[(NH_3)_5Ru-py]^{2+}$ complex (py = pyridine, λ_{max} = 405 nm)[24] and comparable to the energy observed in the $[(NH_3)_5Ru-dmapy]^{2+}$ complex (dmapy = (dimethylamino)pyridine, λ_{max} = 350 nm).[16] This reflects the influence of a donor group on the pyridine ring and the good electronic communication between this group and the pentaammineruthenium group.

Cyclic voltammetry of $[(NH_3)_5Ru-bphy-Ru(NH_3)_5]^{4+}$ in DMF shows a reversible system at −0.07 V (average for anodic and cathodic peaks). This is assigned to the $Ru^{2+/3+}$ couple. Interestingly, this value is markedly more negative than the value observed with 4,4'-azopyridine (ca. +0.2 V). With respect to 4,4'-azopyridine, this corresponds to a preferential stabilization of ruthenium(III) and shows again the mutual influences of the substituent groups connected to the pyridine ring.

Aerial oxidation of acetone or acetonitrile solutions containing the yellow $[(NH_3)_5Ru-bphy-Ru(NH_3)_5]^{4+}$ complex yielded either the blue complex or the red form depending upon the experimental conditions (neutral or acidic medium). This confirms that the yellow complex obtained with 1,2-bis(4-pyridyl)hydrazine is effectively a reduced form of the blue and red forms obtained from 4,4'-azopyridine. The relations between the different binuclear complexes can be summarized on Figure 7.

Search for an Intervalence Transition through 1,2-Bis(4-pyridyl)hydrazine. Since the two forms $[(NH_3)_5Ru-bphy-Ru(NH_3)_5]^{4+}$ and $[(NH_3)_5Ru-bphy-Ru(NH_3)_5]^{6+}$ have been independently shown to exist, we have tried to prepare the mixed-

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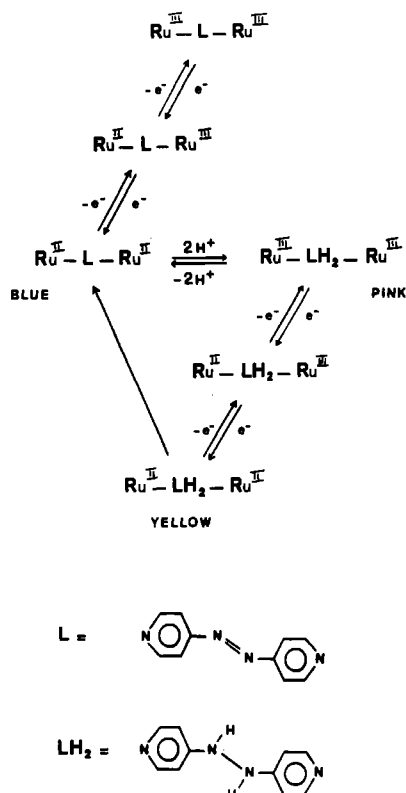
Figure 7. General scheme showing the relations between the different complexes.

valence species in which the two ruthenium atoms are linked by 1,2-bis(4-pyridyl)hydrazine. Thus a solution of the blue 4,4'-azopyridine complex in water (50 mL, 10^{-4} M) was totally converted to the red form by adding HCl (60 μL, 2 × 10^{-1} M). Then, the progressive reduction was performed by adding aliquots of an europium(II) solution.[12] During the reduction, the red color fades and turns to yellow; the band at 490 nm characteristic of the ligand-to-ruthenium(III) charge transfer disappears, whereas the band at 380 nm corresponding to ruthenium(II)-to-1,2-bis-(4-pyridyl)hydrazine charge transfer appears. In the range 1100–1300 nm, a much weaker band is observed; its optical density increases and then decreases, and it completely disappears when 2 equiv of reducing agent have been added. The apparent extinction coefficient (i.e. related to the total concentration of dimers) for this band does not exceed 20 mol^{-1} L cm^{-1}. Thus, assuming that a mixed-valence compound is formed as for the 4,4'-azopyridine complex, the titration experiment shows that its intervalence transition is much weaker than in the previous case. In the limiting case of a comproportionation constant equal to the statistical limit (i.e. 4), the extinction coefficient would be about 40 mol^{-1} L cm^{-1}.

Electronic Interaction through 4,4'-Azopyridine and 1,2-Bis-(4-pyridyl)hydrazine. It is usual to characterize the electronic interaction in mixed-valence complexes by an effective coupling parameter denoted here as V_{ab}. This reduces the complicated chemical structure to an equivalent two-level system and assumes that the experimental effects are the same as if two metal orbitals interact directly through space, with a coupling matrix element V_{ab}. It can then be shown that the intensity of the intervalence band is proportional to the square of this effective electronic coupling parameter.[15] Thus, a strong decrease in the band intensity means that the electronic interaction has been greatly reduced. We have tried to reproduce this gross evolution by an extended Huckel calculation, using a procedure and parameters already described.[25] The V_{ab} parameter was taken from the value of the splitting between the two orbitals with π symmetry and strong metal contributions.

We have first compared the effective couplings in the 1,2-bis(4-pyridyl)ethylene and 4,4'-azopyridine complexes using standard angles (i.e. 120° for the sp^2 atoms) and planar geometry. The choice of a planar geometry could be questioned in both cases: for 1,2-bis(4-pyridyl)ethylene, the steric interaction between the hydrogens of the pyridine ring and of the central CH=CH group are expected to slightly twist the molecule.[26] For 4,4'-azopyridine, these interactions do not exist, but the lone pair of each central nitrogen could lead also to a twist by conjugating with the rings.[7] However, the departures from planarity are expected to remain small, so that in the absence of reliable experimental values, the comparison has been performed here with planar geometries.

For the 4,4'-azopyridine complex, the V_{ab} coupling is found to be 0.097 eV versus 0.043 eV in the 1,2-bis(4-pyridyl)ethylene complex. This marked increase is in qualitative agreement with the experimental behavior. But from the point of view of the interpretation, it incorporates two effects: the change in electronic structure, with the replacement of carbon atoms by more electronegative nitrogen atoms, and the change in bond lengths, the main effect coming from the N=N bond (1.23 Å), which is markedly shorter than the CH=CH bond (1.35 Å). If the effective coupling is computed for an 4,4'-azopyridine complex exhibiting the same bond lengths as 1,2-bis(4-pyridyl)ethylene, the value 0.059 eV is obtained. The gain with respect to 0.043 eV represents the true effect of the change in electronic structure. It is due to the stabilization of the ligand LUMO; this decreases the energy of the radical anion states of the type $Ru^{III}–L^-–Ru^{III}$, which are involved in the strength of the coupling. Changing the bond lengths to their correct experimental values increases then the coupling from 0.059 to 0.097 eV. Thus, according to this simple model, the difference between 1,2-bis(4-pyridyl)ethylene and 4,4'-azopyridine as bridging ligands would come largely from a geometrical effect.

In the case of 1,2-bis(4-pyridyl)hydrazine, assuming first a planar geometry, one gets V_{ab} = 0.033 eV. As above, this variation integrates two effects: the change in electronic structure when the N=N group is replaced by NH—NH and also the change in bond length, because the N—N distance is longer than that in 4,4'-azopyridine. But the result of this calculation is not enough to explain the large experimental difference between 4,4'-azopyridine and 1,2-bis(4-pyridyl)hydrazine, and there is certainly an additional geometric effect. The exact geometry of 1,2-bis-(4-pyridyl)hydrazine is unknown. But according to the literature on substituted hydrazines,[27] its geometry can differ from planarity in two respects. The first (i) results from a pyramidalization of the central nitrogens; in fact this is unlikely to occur here and it would not change dramatically the orbital overlaps (ii) by a torsion around the central N—N bond. Whereas in 4,4'-azopyridine the central part, i.e. the –N=N–moiety, is planar, in the case of substituted hydrazines, it is well-known that a *gauche* conformation is achieved by rotation around the central N—N bond. Usually, the corresponding dihedral angle is around 90°, which would explain the very low effective coupling.

Conclusion

The 4,4'-azopyridine/1,2-bis(4-pyridyl)hydrazine system appears as an interesting system to test the possibility of control of an intramolecular electron transfer by a chemical reaction. The experimental characterization of the coupling is made difficult, because of the extensive overlap between the intervalence band and the metal-to-ligand charge-transfer band, but the use of other metallic sites, presently under investigation, could improve the band resolution. Finally, such compounds raise the important problem of the exact molecular conformation in solution. Theoretical work is also in progress in this direction.

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