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Electrochemistry of $[(Ru(bpy)_2)_2bpm](PF_6)_4$. Complete Assignment of Individual Reduction Steps

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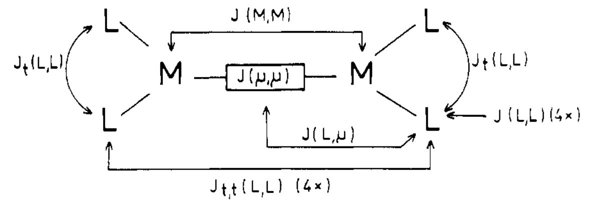
$[(Ru(bpy)_2)_2bpm]^{4+}$ (**1**) was shown to undergo 14 one-electron processes at the electrode—two Ru-based oxidations and twelve ligand-based reductions. Unlike the case of other mononuclear Ru–bpm complexes, in **1** the bridging bpm ligand is reduced in two one-electron steps to the dianion before reduction of the terminal bpy. After the first stage of reduction of all the bpy ligands, the next reduction is one involving the second LUMO of μ-bpm. The reduction of bpm is completed by a second one-electron process at more negative potentials only after all bpy ligands undergo reduction to bpy^{2-}. The products of the reduction up to the 3– species are fairly stable; however, the products of more negative processes undergo decomposition within the time scale of the CV method. All electron repulsion interactions, as reflected in the $\Delta E°$ values, were identified, and it was shown that the μ-bpm ligand transmits electronic effects in unreduced as well as in reduced form. The fact that the first two electrons are accepted by bpm before the reduction of bpy is discussed in terms of fully symmetrical coordination of bpm.

Introduction

Bi- and polynuclear bridged complexes containing one or more redox-active metal centers have attracted much interest in the last 10–15 years. Most of the attention has been directed toward Ru–polypyridine complexes, but recently Os and Re species have also been studied. Photophysical and photochemical properties have mostly been investigated, complemented in many cases by electrochemical studies (for selected relevant papers see ref 1). The increasing interest is connected with the possibility of using these compounds as components of more complex systems capable of intramolecular electron transfer and thus forming blocks in photochemical molecular devices. Furthermore, their ability to undergo multielectron changes predetermines them as mediators or electron-transfer catalysts with tunable redox properties. Recently, the possibility of also using them as photoelectrochemical units in molecular electronic devices has been discussed.[2]

Most electrochemical studies deal predominantly with metal–metal interactions mediated through the bridging ligand. Only a few recent papers describe some of the reduction processes, however, not in full detail and without any thorough analysis of the processes.[3] Not in one single case, to our knowledge, has a complete set of all possible reduction steps been described and analyzed. The reduction processes carry a wealth of information regarding the electronic interactions taking place in these complexes, mainly between ligand-based redox centers. Most of the species formed in the ligand-based reductions contain unpaired electrons so that any further reduction is influenced by the interaction between an incoming electron and the already present unpaired electron(s). In cases where the redox-active centers are bound to different metal atoms, the effects of these interactions are transmitted through the bridge ligand, so that actually we are dealing with mixed-valence states, however, ligand localized and thus also more spatially distant. For these reasons, the magnitude of interaction is usually smaller, though detectable. Interactions among electrons localized on ligands bonded to the same metal atom are expected to be of about the same magnitude as those in mononuclear complexes.

Scheme I



The knowledge of these ligand–ligand interactions opens new possibilities of using these reduced species as multielectron-transfer agents and as units in molecular electronic devices. The prerequisite for complete analysis of these ligand–ligand interactions is the determination of the localization of electron changes in the individual redox steps that are observed. This cannot be achieved solely by using electrochemical methods so that a combination of techniques, mainly electrochemical and spectroelectrochemical, is necessary to obtain the desired information.

Scheme I depicts the main possible electron repulsion interactions taking place in the symmetrical bridged species $L_2M\text{-}\eta\text{-}L\text{-}ML_2$.

$J(M,M)$ denotes the interaction between the metal centers, mediated through the bridging ligand and/or occurring directly between the metals through space (e.g. δ-bonding). $J(\mu,\mu)$ is the spin-pairing interaction in the bridging ligand. $J(L,L)$ represents the analogous interaction in the individual ligands (intraligand interaction). $J_t(L,L)$ is the interligand interaction between ligands bound to the same metal atom, whereas $J_{t,t}(L,L)$ is the analogous interaction among terminal ligands bound to different metal

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centers. Furthermore, the term $J(L,\mu)$ might also play a role in cases where reduction of the bridge is situated between reductions of terminal ligands. The predicted order of magnitudes of the various interactions is $J(\mu,\mu)$, $J(L,L) > J(M,M) \geq J_t(L,L) \geq J(L,\mu) > J_{t,t}(L,L)$. Electrochemically these J values are not directly accessible, because only differences in half-wave potentials are measured experimentally. The latter are related to the above J terms by the relation (generally)[4]

$$\Delta E_{1/2} \approx J + \Delta E_s \qquad (1)$$

(J terms are always positive, whereas ΔE_s—the change of solvation energy—is negative); i.e., the $\Delta E_{1/2}$ values reflect the electron interaction energy corrected for the corresponding change in solvation energy.[5,6] The latter can be regarded as more or less constant within the redox series.[7] However, this approximation is not always valid.[6,8] Nevertheless, the changes in $\Delta E_{1/2}$ can be taken as roughly reflecting the changes in magnitudes of the repulsion terms when certain conditions are being met.[8]

For our study of the reduction pattern of bridged complexes, we have chosen $(bpy)_2Ru$-μ-bpm-$Ru(bpy)_2{}^{4+}$ (**1**) (bpy = 2,2'-bipyridine, bmp = 2,2'-bipyrimidine). This compound was first described by Hunziker and Ludi,[9] who also gave values for the ruthenium oxidation potentials. The complex was reinvestigated several times;[10] however, the Ru oxidation was again the main focus of study. In ref 10d, the reduction of the bridging ligand and a few terminal ligands is described and the EPR spectrum of the first reduction product is given, as is also found in ref 10e.

1 can be expected, on the basis of the number of accessible redox orbitals, to exchange at least twelve electrons (two on the Ru atoms, two on the bridging ligand, and eight on the terminal bpy ligands). However, EHMO calculations[11] indicate a rather low-lying second LUMO in 2,2'-bipyrimidine which could be expected to be stabilized by the influence of the two $Ru(bpy)_2$ groups to such an extent that its redox activity might become apparent in the accessible potential range and thus one or two more reduction steps could be expected (cf. e.g. the reduction of ligated 4,4'-diphenyl-2,2'-bipyridine with a similarly located second LUMO[12]).

Experimental Section

Reagents. *N,N*-Dimethylformamide (DMF), tetrabutylammonium hexafluorophosphate ($(TBA)PF_6$), 2,2'-bipyridine (bpy), and 2,2'-bipyrimidine (bpm) were used and purified as described in a previous paper.[13] Acetonitrile (Fluka, spectral grade) (AN) was dried and purified by storing over 4A molecular sieves for 2 weeks, stored over P_2O_5 for 3 days, and then distilled, refluxed over CaH_2 for 1 day, and finally fractionally distilled. All operations were carried out under argon atmosphere. Both solvents were distilled in a closed system directly into the electrochemical cell or Schlenk vessel containing predried depolarizer and supporting electrolyte. $RuCl_3 \cdot xH_2O$ (Fluka) was used without further purification.

Preparation of Complexes. $\mathbf{Ru(bpy)_2Cl_2 \cdot 2H_2O}$. The complex was prepared by the method of Sullivan et al.[14]

$\mathbf{[(Ru(bpy)_2)_2bpm](PF_6)_4}$. The complex was prepared by the method of Hunziker[9] with the following modifications.[16] A mixture of $Ru(bpy)_2Cl_2 \cdot 2H_2O$ and bpm (2:1) was refluxed in 20 mL of ethylene glycol for 45 min. The solution was cooled to room temperature and filtered. The complex was precipitated by adding an aqueous, saturated solution of KPF_6. A 20-mL portion of water was added, and the mixture was filtered. The precipitated complex was dried, dissolved in a small amount of AN, and again precipitated by pouring into excess diethyl ether.

Finally, the complex was purified by chromatography.[4] The green band was collected, and the complex was precipitated and dried as described above.

Physical Measurements. Procedures and apparatus were described previously.[13] Products of electrode reactions were generated electrochemically in an optically transparent thin-layer electrode (OTTLE) cell of new construction[13b] which made it possible to carry out the electrolysis and spectral measurement with complete exclusion of oxygen and moisture. DPP (differential-pulse polarography) curves, eliminating

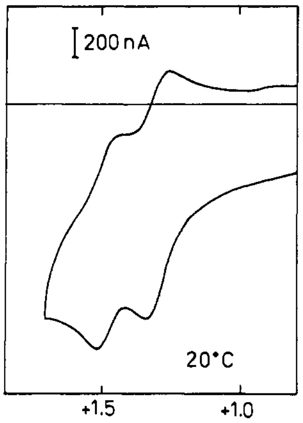

Figure 1. Oxidation of **1** at a Pt electrode (AN; 0.1 M $(TBA)PF_6$; 100 mV/s; 20 °C).

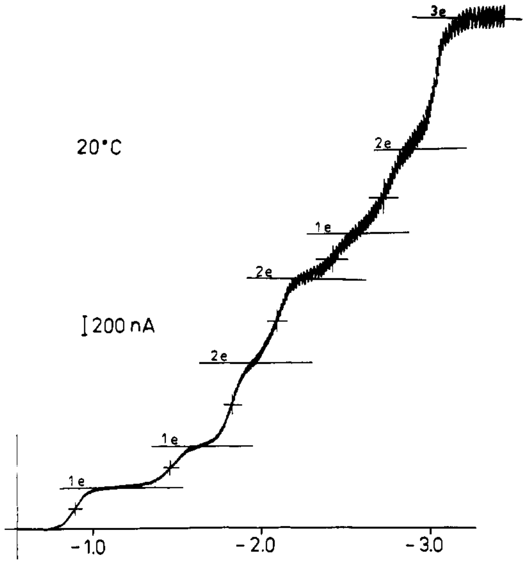

Figure 2. Reduction of **1** at a dropping-mercury electrode (DMF; 0.1 M $(TBA)PF_6$; 20 °C).

Table I. Reduction of **1** at the DME in DMF, 0.1 M $TBAPF_6$ (Room Temperature)[a]

wave	$E_{1/2}$, V	slope, mV	n
1	−0.88	80	1
2	−1.45	100	1
3	−1.84	84	2
4	−2.09	120	2
5	−2.46	150	1
6	−2.76	(114)	2
7	−3.03		3[b]

[a] $E_{1/2}$ given with reference to the Fc/Fc^+ couple. [b] Not a well-resolved three-electron process.

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(4) This holds for successive reductions of a ligand system with identical ligands. For a heteroleptic coordination sphere, differences in orbital energies enter eq 1.

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Table II. CV Characteristics of **1** at a Pt Electrode in AN and DMF, 0.1 M (TBA)PF_6[a]

	20 °C					-75 °C, DMF			
	AN		DMF						
peak	E_p^c, V	ΔE_p, mV	E_p^c, V	ΔE_p, mV	chem rev	E_p^c, V	ΔE_p, mV	chem rev	*n*
1	+1.36	65			+				1
2	+1.18	65			+				1
3	−0.79	60	−0.93	90	+	−0.97	60	+	1
						−1.05	60		
4	−1.48	60	−1.50	60	+	−1.54	50	+	1
5			−1.95	95	+	−1.95	75	+	2
6			−2.19	65	+	−2.16	55	+	2
7			−2.33	60	+	−2.27	60	+	1
8			−2.80		irr	−2.71		irr	2
9			−3.13		irr	−2.92	60	+	2
10					−	−3.01		irr	1
Fc			0	65	+	0	45	+	

[a] Peak potentials given with reference to Fc/Fc^+ couple. *n* = number of electrons exchanged in a given step.

charging current, were recorded using a dropping-mercury electrode as a working electrode, silver wire as a quasireference electrode, and a platinum plate as a counter electrode. All potentials are referred to the ferrocene–ferrocenium (Fc/Fc^+) couple taken as zero at all temperatures and in all solvents. Potentials are given as cathodic peak potentials because the anodic counterpart of the CV curve did not appear in all cases. Dc potentials at the dropping-mercury electrode are given as half-wave potentials referred to the Fc/Fc^+ couple. The reproducibility of peak and half-wave potential was about 25 mV; the differences in potentials were reproduced to about 10 mV.

As noted previously, the evaluation of the ratio of cathodic and anodic peak currents is extremely difficult for multielectron processes and can be carried out reliably only for well-separated waves (in this specific case for the first and second reduction steps). Simulation of the observed curves is also impossible for the full range of the CV curve, so only model simulations for specific parts of the curve were made. The determination of the number of electrons exchanged in individual steps was based mainly on measurements made with the dropping-mercury electrode.

Results

Complex **1** shows two one-electron anodic oxidations (see Figure 1 and Table II) at rather positive potentials, as already described.[9,10] The waves are both chemically and electrochemically reversible, with the difference of half-wave potentials being 0.18 V in acetonitrile at ambient temperature.

Dc polarography at the DME in DMF at ambient temperature reveals, within the available potential window, seven reduction waves corresponding to the acceptance of a total of 12 electrons per one molecule (see Table I and Figure 2). The first two waves each correspond to a one-electron process. They are followed by a set of two waves, each corresponding to a two-electron process, the slopes of which are, however, rather large (see Table I). This set is followed by a rather broad one-electron wave. The remaining two waves correspond to two- and three-electron processes, respectively, again with rather high slopes. The measurements made with the DME at potentials more negative than −2.0 V were shown to be dependable with regard to the number of exchanged electrons. However, pulse techniques applied to the DME in DMF have shown adsorption and film formation at the electrode which influence strongly the shapes of the waves and partly the half-wave potentials. Nonfaradaic peaks are formed in this region by DPP, in some cases connected with a negative DPP response. As these adsorption phenomena have no specific correlation with the problem studied, they were not investigated in detail. The DME measurements were used only to establish the overall number of electrons in the individual steps.

The dc picture is essentially reproduced in the CV curve (see Table II for data and numbering scheme for the electrode reactions). The first five reduction steps are chemically reversible; however, only steps 4 (see Figure 3) and 7 show the expected differences of cathodic and anodic peak potentials corresponding to electrochemical reversibility. Step 8 is both electrochemically and chemically irreversible at ambient as well as at low temperature; step 9 is irreversible at ambient temperature and becomes chemically reversible only at low temperature. The last step, 10, separates from step 9 only at low temperature and seems to be chemically irreversible even at these low temperatures. Steps 9 and 10 correspond to the last, three-electron, wave observed under dc conditions at the DME. The model simulations of the CV curve confirm the number of electrons observed by dc polarography for the set of steps 5–7 and indicate that steps 9 is a two-electron whereas step 10 is a one-electron process.

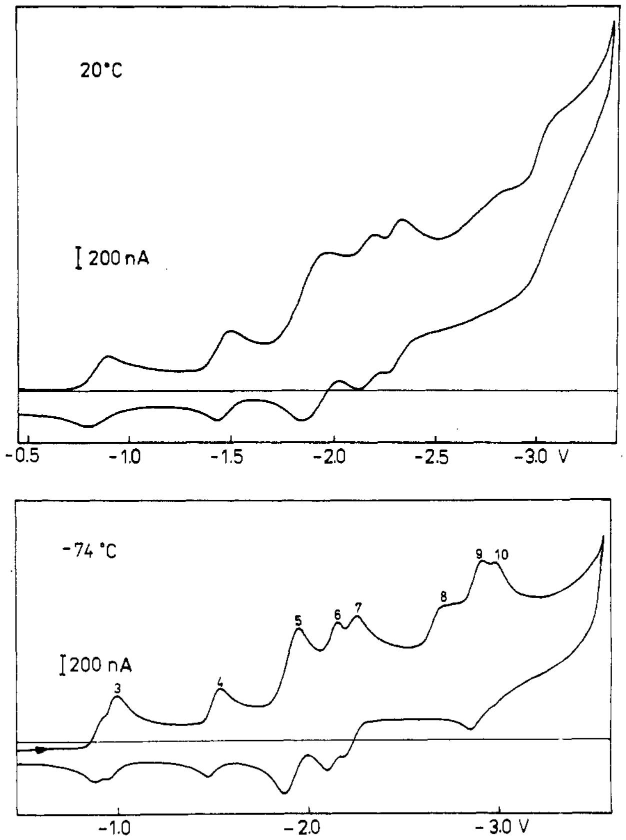

Figure 3. Reduction of **1** at a Pt electrode at 20 and −74 °C (DMF; 0.1 M (TBA)PF_6; 100 mV/s; first cycle only).

The peak potentials do not depend upon the scan rate (50–1000 mV s^{-1}), with the exception of peaks 8 and 10, which shift by about 100 mV to more negative potentials with a 10-fold increase in scan rate; the ratio of peak currents remains essentially constant with scan rate as well as with temperature, and the general pattern of steps is also independent of scan rate.

To identify the products of individual electrode processes, UV–vis spectra were measured in an OTTLE cell. The results are given in Figure 4 and Table III, in which also the tentative assignments of individual transitions are indicated.

It was shown that the spectra of electrochemically prepared reduction species can be taken only up to step 6. Step 7 is located

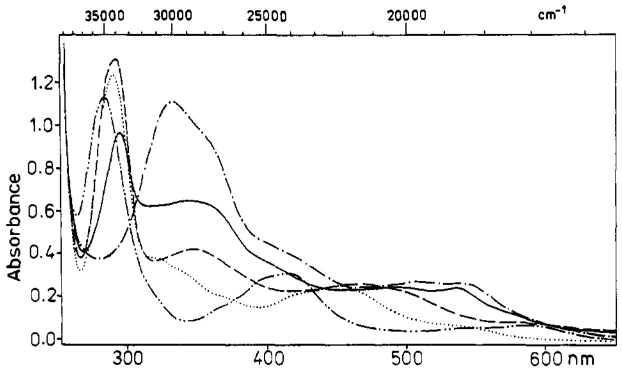

Figure 4. UV-vis spectra of **1** and its reduction products taken in an OTTLE cell (DMF; 0.1 M $(TBA)PF_6$): original species (–··–); product of one-electron reduction (···); product of two-electron reduction (– –); product of four-electron reduction (—); product of six-electron reduction (–·–).

Table III. UV–Vis Characteristics of **1** and Its Reduction Products in DMF[a]

n	ν, cm⁻¹	$10^4\epsilon$	tentative assgnt
0	34 960	7.13	$\pi \rightarrow \pi^*$ (bpy, bpm)
	26 595	sh	
	24 752	sh	M → L (bpy, bpm)
	23 923	1.99	
	18 380		
	17 065	0.61	M → L (bpm)
−1	34 480	7.80	$\pi \rightarrow \pi^*$ (bpy)
	31 250	2.39	$\pi \rightarrow \pi^*$ ($bpm^{\bullet-}$)
	25 590	sh	
	27 174	sh	
	23 810	1.30	
	22 124	1.55	M → L (bpy)
	18 450	0.33	M → L ($bpm^{\bullet-}$?)
−2	34 250	8.19	$\pi \rightarrow \pi^*$ (bpy)
	28 740	2.63	$\pi \rightarrow \pi^*$ (bpm^{2-})
	26 320	sh	
	21 460	1.59	M → L (bpy)
	19 920	sh	
	17 180	0.53	
−4	33 785	5.45	$\pi \rightarrow \pi^*$ (bpy)
	29 070	3.62	$\pi \rightarrow \pi^*$ ($bpy^{\bullet-}$) $\pi \rightarrow \pi^*$ (bpm^{2-})
	27 624	sh	
	24 040	sh	
	20 171	1.29	$\pi \rightarrow \pi^*$ ($bpy^{\bullet-}$)
	18 660	1.29	$\pi \rightarrow \pi^*$ ($bpy^{\bullet-}$)
−6	29 940	6.24	$\pi \rightarrow \pi^*$ ($bpy^{\bullet-}$) $\pi \rightarrow \pi^*$ (bpm^{2-})
	27 624	sh	
	23 697	sh	M → L ($bpy^{\bullet-}$?)
	19 610	1.53	$\pi \rightarrow \pi^*$ ($bpy^{\bullet-}$)
	18 520	1.48	$\pi \rightarrow \pi^*$ ($bpy^{\bullet-}$)

[a] *n* = number of accepted electrons. OTTLE cell; 0.1 M $(TBA)PF_6$; 20 °C.

very close to the preceding step, and the results are thus not reliable. Products of all other more negatively located reduction steps are not of sufficient stability to make it possible to investigate them on a time scale larger than about 1 s. This excluded electrolytic preparation and, consequently, also spectroelectrochemical investigation of these highly reduced species.

Discussion

Electrochemistry. The difference in half-wave potentials corresponding to Ru oxidations, 0.18 V, leads to a rather high comproportionation constant, $K_{com} = 1.1 \times 10^3$, indicating that the mixed-valence state is table. The positive values of the oxidation potentials (about 300 mV more positive for the first oxidation of **1** as compared with $Ru(bpy)_3^{2+}$) reflect the electron-withdrawing power of the bridging ligand, which is greater than that exerted in the corresponding mononuclear species (cf. $Ru(bpy)_2bpm^{2+}$ oxidation at +1.0 V vs the Fc/Fc^+ couple).

Evaluation of the experimental data for the reduction steps, using the usual diagnostic criteria, leads to the conclusion that all 12 electrons are accepted by the parent species in a multielectron sequence of redox processes and excludes the ECE mechanism as well as the branched ECE mechanism, i.e.

$$\begin{tikzcd}
A \arrow[r, Leftrightarrow] & B \arrow[r, Leftrightarrow] \arrow[d] & C \\
 & D \arrow[r, Leftrightarrow] & E
\end{tikzcd}$$

(II)

It can thus be concluded that the multielectron reduction is localized primarily on the parent particle of **1**, and we observe total reduction of the coordinated ligands, the bridging ligand being most probably reduced to its 4− state. If there are some coupled chemical reactions, as seems to be the case in the region of steps 8–10, they lead to electrochemically inactive species.

The first two reduction waves, steps 3 and 4, were ascribed on the basis of electrochemical considerations and EPR studies to the reduction of the bridging ligand.[10d] In the UV-vis spectra, after one electron per particle is accepted, there are two features ascribable to coordinated $bpm^{\bullet-}$: a band at 31 050 cm⁻¹, with two shoulders at longer wavelengths, and a band at 22 100 cm⁻¹, with a shoulder at 23 800 cm⁻¹. These bands can be compared with those of free $bpm^{\bullet-}$ at 26 950, 19 530, and 18 180 cm⁻¹ and those of $bpm^{\bullet-}$ ligated to only one $Ru(bpy)_2$ unit, which appear at 29 410 and 20 530 cm⁻¹, respectively.[15] The dominant band, typical for most monoanion radicals of polypyridines, around 30 000 cm⁻¹, is in the case of **1** partly obscured by the sharply rising band of bpy (see Figure 4); however, it can be unambiguously identified. There are no features in the spectra which would correspond to $bpy^{\bullet-}$. The combined evidence thus points to the conclusion that the first reduction is localized on the bridging ligand. When the second electron is added, the spectrum changes, showing new bands at 28 990 and 21 650 cm⁻¹. These bands cannot be compared either with analogous bands of free doubly reduced bpm or with those of the mononuclear species. In the former case, the band observed at 23 260 cm⁻¹ corresponds to the biprotonated species[13] whereas, in the latter case, reduction of bpy seems to precede the second reduction of bpm.[15] However, as there are no features attributable to reduced bpy in the spectra, especially no decrease of the bpy band at 34 130 cm⁻¹, it is very reasonable to assume that the newly observed bands arise from coordinated bpm^{2-}; i.e., the second electron is also localized on the bridging ligand.

The first reduction, step 3, is however solvent dependent: In AN it is located at −0.79 V and has all characteristics of an electrochemically as well as chemically reversible wave (the ratio of cathodic and anodic peak currents, which equals 1.06 (ΔE_p = 60 mV), does not depend upon sweep rate). In DMF the peak potential of the step is shifted by about 0.14 V to more negative potentials and, the reduction being chemically fully reversible, the corresponding ΔE_p increases to 90 mV at a sweep rate of 100 mV s⁻¹. An analogous result is obtained under dc conditions at the DME in DMF, the wave having a slope of 85 mV at room temperature. When the temperature is lowered to −75 °C in DMF, the wave splits into two separate peaks (see Table II and Figure 3). Both are chemically as well as electrochemically reversible, and their sum corresponds to the acceptance of one electron. These results point to the conclusion that the apparent electrochemical irreversibility at ambient temperatures in DMF is due to poor resolution of two very close steps. These two close processes seem to correspond to the reduction of two interrelated forms of **1** present in DMF solution. It would be very tempting to ascribe these two peaks to the reduction of diastereomers which have to exist in this type of compound.[17] However, the strong solvent dependence of the behavior casts some doubt on this seemingly most probable explanation. The nature of the forms

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(17) (a) Ernst, S.; Kasack, V.; Kaim, W. *Inorg. CHem.* **1988**, *27*, 1146. (b) Ernst, S.; Kaim, W. *Inorg. CHem.* **1989**, *28*, 1520.

being reduced and the solvent dependence are under more detailed investigation.

The following two steps each correspond to a two-electron reduction. The characteristics of the dc as well as of the CV patterns do show complete chemical reversibility, albeit their electrochemical parameters (slope of dc curve and ΔE_p of CV peaks) seem to indicate an electrochemically complicated process. The UV–vis spectra show features typical of $bpy^{\bullet -}$ reduction: At potentials corresponding to the formation of the zero-charged complex (i.e., four electrons accepted per particle), a decrease of the typical bpy band at 33 450 cm^{-1} is observed and a new band at 30 000 cm^{-1} and a characteristic "double" band with maxima at 19 800 and 18 500 cm^{-1} are formed. These bands indicate formation of coordinated $bpy^{\bullet -}$.[18] As the process is a two-electron one, it must be attributed to terminal bpy molecules ligated to different Ru atoms. The slope and ΔE_p thus do not reflect electrochemical irreversibility but are due to two poorly resolved processes. The theory developed for semiquinone formation[19] is fully applicable to the corresponding dc wave, as is the treatment of CV peaks by Richardson and Taube.[20] The corresponding value for the difference of redox potentials of the reduction of the two identical terminal bpy ligands, reflecting the mutual interelectronic interaction $J_{t,t}(L,L)$, is about 60 mV.

The second two-electron reduction, being chemically fully reversible, shows a similar behavior: the slope of its dc curve is greater than that of a reversible electrochemical process, as is the value of ΔE_p. The UV–vis spectra show a complete disappearance of the bpy band at about 33 500 cm^{-1}, and the band attributable to $bpy^{\bullet -}$ is fully developed and has all the typical characteristics of a ligated $bpy^{\bullet -}$ band. The same holds for the "double" band, located in this case at 19 600 and 18 350 cm^{-1}, respectively. The latter is partly obscured at shorter wavelengths by the underlying absorption of bpm^{2-}. The process is thus the reduction of remaining terminal bpy ligands. The interelectronic interaction $J_{t,t}(L,L)$ is in this case, however, decreased, when compared with the preceding reaction, the difference in corresponding $E_{1/2}$ values being only about 35 mV. This assignment is confirmed also by the difference in half-wave or peak potentials between this step and the preceding one. This difference should correspond to interligand electron repulsion between bpy on the same metal atoms, $J_t(L,L)$, and amounts to 0.24 V, a value comparable with that for $Ru(bpy)_3^{2+}$, 0.19 V, as predicted by the theory of redox series.[6,8]

All the more negatively located reduction steps were studied only electrochemically, as it was established that the products formed are not of sufficient stability.

The reduction resulting in complete formation of terminal $bpy^{\bullet -}$ is located at −2.16 V. The next reduction should be shifted by the amount reflecting the spin-pairing energy in the bipyridine ligand, i.e. by about 0.6–0.7 V.[8] We find a two-electron reduction wave (step 8) at −2.71 V followed at −2.92 V (step 9) by the second two-electron wave. These differences in half-wave potentials do follow the expected pattern of a bpy-based redox series,[8] so that these two reduction steps can be ascribed to the reduction of terminal bpy ligands forming bpy^{2-}. It is interesting to note that the first of these two steps is chemically irreversible whereas the second shows a certain degree of chemical reversibility. It has to be also recalled that the peak potential around −2.7 V is scan rate dependent, the second being more or less constant with scan rate. This sort of behavior is typical for the mechanism

$$\begin{tikzcd} A \arrow[r, Leftrightarrow] & B \arrow[r, Leftrightarrow] \arrow[d] & C \\ & I & \end{tikzcd} \qquad \text{(III)}$$

(I denotes an electroinactive species). The species with only two bpy^{2-} ligands is rather unstable and decomposes rapidly, resulting in a chemically irreversible step. However, when more negative potentials are approached, the newly formed species with all bpy being in the form of bpy^{2-} is much more stable, resulting in a partially chemically reversible reduction. The simulation of mechanism III shows that this sort of behavior actually results. The instability of the species with only one terminal bpy on each Ru atom reduced might be ascribed to the asymmetry of the coordination sphere, which would make complex more susceptible to substitution. As there are no indications of any oxidation (or reduction) of the decomposition product, the simple splitting off of the reduced ligand seems to be excluded. More probably, protonation by the solvent (DMF) takes place, leading to products electroinactive in the given region of potentials.

However, there remain two more waves to be identified—steps 7 and 10. They are both one-electron reductions, the first one at −2.27 V being fully reversible, chemically and electrochemically. The second seems to be irreversible. However, under extremely dry conditions, there is an indication of the reverse anodic peak. These two waves cannot be ascribed to bpy ligands, as the number of electrons as well as the location of the waves, as shown above, is fully out of the expected pattern of the redox series formed by bpy ligands. The difference in potentials between the two waves (about 0.74 V) indicates a reduction localized on one redox orbital. The only possibility seems to be the reduction of the bridging ligand, bpm, using its higher redox orbital. This redox orbital should be located about 0.6–0.7 V above the LUMO, as indicated by EHMO calculations.[11] The difference between the second reduction of bpm, forming its dianion, and the reduction under consideration is about 0.75 V, in rough agreement with the calculated difference. The pairing energy, reflected in the difference between steps 7 and 10, is of the correct magnitude expected for such a system carrying rather negative overall charge. This electrochemical reasoning, based on the analysis of the pattern of the redox series, leads to the conclusion that steps 7 and 10 actually correspond to the reduction of bpm, forming in the end bpm^{4-} as the bridging ligand. The second redox orbital of bpm becomes available with strong ligation to two Ru atoms. The reductions of free bpm, of bpm ligated to one $Ru(bpy)_2$ unit, and of bpm bound to two $Ru(bpy)_2$ units are located at −2.34, −1.44, and ∼≈−1.00 V, respectively. However, as there is no indication of the use of the second redox orbital of bpm ligated asymmetrically to one $Ru(bpy)_2$ unit, it has to be concluded that the great shift of the second redox orbital of bpm is due to the symmetrical coordination of two $Ru(bpy)_2$ units, which decreases the energy of the second redox orbital, with respect to that of the first one, to a greater extent than does the coordination of one $Ru(bpy)_2$ unit. Preliminary calculations, carried out in this laboratory, do not contradict this conclusion.

To summarize the discussion, it is possible to write for the reduction of **1** the sequence shown in Scheme II.

Electronic Spectra. The specific changes in the spectra were described above when the assignment of individual redox steps was discussed. There are, however, some general features that must be mentioned, as they are observed with other heteroleptic compounds also.

The band for the nonreduced species **1** located at 34 960 cm^{-1} and assigned unambiguously to the $\pi \rightarrow \pi^*$ transition of bpy (and partially of bpm) shifts with the reduction of other ligands to longer wavelengths and increases in intensity. For the species reduced with one electron, when the underlying bpm absorption disappears, its intensity increases from 7.13×10^4 to 7.8×10^4 M^{-1} cm^{-1} with a simultaneous shift from 34 960 to 34 480 cm^{-1}. For the species with fully reduced bpm, the extinction coefficient increases to 8.19×10^4 M^{-1} cm^{-1} and the band position shifts to 34 250 cm^{-1}. This shift in position continues with partial reduction of bpy itself, reaching 33 785 cm^{-1} with half of bpy ligands present being reduced. This shift in position was also found for the reduction of $Ru(bpy)_3^{2+}$ [18] and for most heteroleptic complexes with ligands more easily reducible than bpy.[21] This indicates that the ligands in the complexes under consideration do not behave completely independently; the influence of the change in charge density in one ligand is transmitted to unreduced ligands, making the transition energetically easier (by changing the orbital energy of

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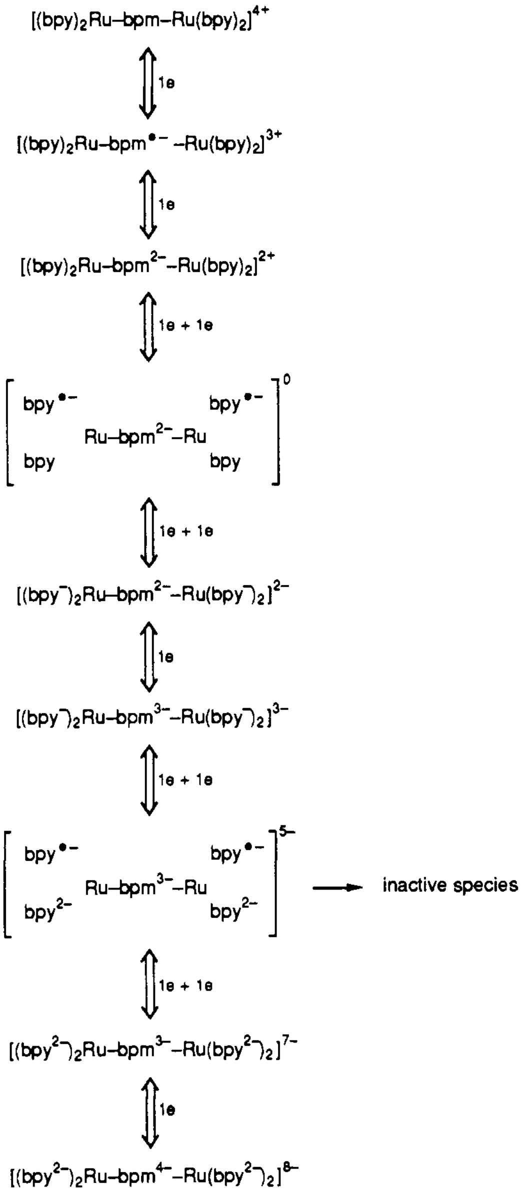
(18) Heath, G. A.; Yellowlees, L. J.; Braterman, P. S. *J. Chem. Soc., Chem. Commun.* **1981**, 287.
(19) Brdička, R. *Z. Elektrochem.* **1941**, *47*, 314.
(20) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

Scheme II



unreduced bpy) and, more importantly, increasing the probability of spectral transition by increasing the coupling (direct or indirect via Ru atoms) between the ligands in the partially reduced complexes. In the specific case discussed here, the influence of the reduction of the bridging ligand upon the $\pi \rightarrow \pi^*$ transition of bpy shows clearly that the transmission of the electronic effect takes place between the bridging ligand and the terminal ones. The spectra for species with four or six accepted electrons closely resemble those of simple bpy complexes. The underlying absorption of the reduced bpm is of rather low intensity, and its effect is manifested only in some parts of the spectra where the low-intensity bands of bpy are not so well developed as, e.g., in the Ru(bpy)$_3^{2+}$ species. However, the presence of underlying absorption has to be kept in mind, especially when one is comparing the intensities or attempting to assign some of the shoulders to specific transitions.

The assignment of the transitions given in Table III has been made by comparing spectra of **1** with those of free ligands and their reduction products and those of similar complexes, i.e. Ru(bpy)$_3^{2+}$, Ru(bpm)$_3^{2+}$, and Ru(bpy)$_2$bpm^{2+} and their reduced species.[18,21] Especially for the reduced species, there is no other approach possible which could support the given assignments. The solvatochromic effect, if any, is rather weak and does not help in identifying the individual transition. E.g., for the unreduced species **1**, the values observed for the bpy (bpm) $\pi \rightarrow \pi^*$ band, which is the most sensitive to the solvent effect, are 35 970 cm^{-1} (H$_2$O), 35 210 cm^{-1} (MeOH), 34 960 cm^{-1} (DMF), and 35 715 cm^{-1} (AN), respectively.

Concluding Remarks

All the 14 electrons exchanged by **1** with the electrode have been assigned to specific processes using electrochemical and spectroelectrochemical reasoning. All $\Delta E_{1/2}$ values reflecting the interaction terms (eq I) depicted in Scheme I have been determined, with the exception of that for $J(\mu,\mathrm{L})$. They are fully consistent throughout the whole region of redox potentials. The bridge has been shown to transmit the electronic effects both on the anodic side ($J(\mathrm{M,M})$, $\Delta E° = 0.18$ V) and on the cathodic side ($J_{\mathrm{t,t}}(\mathrm{L,L})$, $\Delta E° = 0.04$–0.060 V). The long-distance interaction between bpy ligands is, as expected, weaker than the more direct metal–metal interaction. It is to be noted that the bridging ligand does not lose its transmitting properties even after its two-electron reduction. The $\Delta E_{1/2}$ values for interligand terms, $J_{\mathrm{t}}(\mathrm{L,L})$, are analogous to those observed in other bpy complexes.

The μ-coordination of bpm to two Ru(bpy)$_2$ units changes its behavior considerably when compared with the case of monomeric species, where bpm is coordinated either to a Ru(bpy)$_2$ unit or to a Ru(bpy)bpm unit:[21] The first reduction is shifted by about 0.55 V toward positive potentials. This can be attributed to the influence of two positive charges on the Ru atoms located symmetrically with respect to the bpm molecule. The second important feature is that the second electron is accepted by bpm before the first reduction of bpy. In other species (i.e., Ru(bpy)$_2$bpm^{2+} or Ru(bpm)$_2$bpy^{2+}) this second reduction of bipyrimidine is always inserted between the first and second reductions of bpy;[21] i.e., all the ligands are reduced by one electron before the reduction resulting in spin pairing.[21] However, in the bridged species, the bpm bridge is reduced completely before the reduction of the terminal bpy. The first reduction of bpy is shifted toward negative potentials by about 0.2 V as compared with that for monomeric Ru(bpy)$_2$bpm^{2+}. This shift in the first reduction of bpy, reflecting the change in orbital energy of ligated bpy, is obviously due to the dianionic nature of the bridging ligand, which forces part of its charge density onto both Ru(bpy)$_2$ units, making them less easily reducible. The interligand interaction not only follows from electrochemical data but is also reflected in the UV–vis spectra, as noted above. Even if it is possible to use the localized redox orbital model[8] for description of the behavior of the complex, it is necessary to regard it as an approximation, as the mutual interaction of ligands leads to rather small but detectable changes in the behavior of all components of the complex.

Registry No. I, 65013-24-3; DMF, 68-12-2; AN, 75-05-8; (TBA)PF$_6$, 3109-63-5; Ru(bpy)$_2$Cl$_2$, 15746-57-3; KPF$_6$, 17084-13-8; Pt, 7440-06-4; [(Ru(bpy)$_2$)$_2$bpm](PF$_6$)$_4$, 65013-25-4; [(Ru(bpy)$_2$)$_2$bpm]$^{5+}$, 67113-73-9; [(Ru(bpy)$_2$)$_2$bpm]$^{6+}$, 66859-37-8; [(Ru(bpy)$_2$)$_2$bpm]$^{3+}$, 124561-82-6; [(Ru(bpy)$_2$)$_2$bpm]$^{2+}$, 140697-19-4; [(Ru(bpy)$_2$)$_2$bpm]^{0}, 140697-20-7; [(Ru(bpy)$_2$)$_2$bpm]$^{2-}$, 140697-21-8; [(Ru(bpy)$_2$)$_2$bpm]$^{3-}$, 140697-22-9; [(Ru(bpy)$_2$)$_2$bpm]$^{5-}$, 140697-23-0; [(Ru(bpy)$_2$)$_2$bpm]$^{7-}$, 140697-24-1; [(Ru(bpy)$_2$)$_2$bpm]$^{8-}$, 140697-25-2; mercury, 7439-97-6.

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(21) Krejčík, M.; Vlček, A. A. Prepared for publication.