Spectroelectrochemical and Flash Photochemical Reduction of 1,4,5,8-Tetraazaphenanthrene and 1,4,5,8,9,12-Hexaaza-triphenylene Mono- and Bi-metallic Ruthenium(II) Complexes

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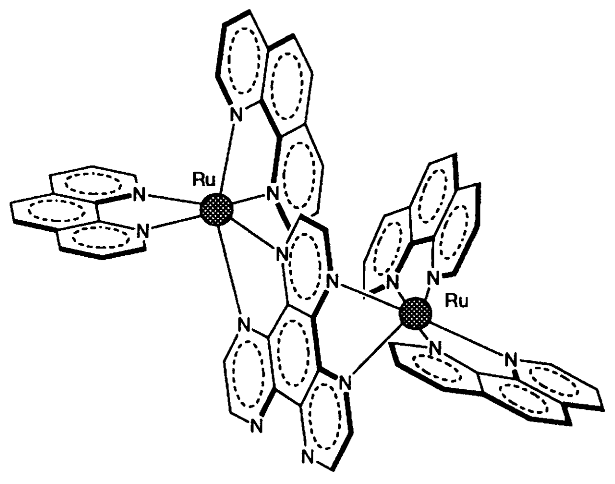
The spectroelectrochemical reduction and photoreduction of $[\{Ru(phen)_2\}_2(hat)]^{4+}$ (phen = 1,10-phenanthroline, hat = 1,4,5,8,9,12-hexaazatriphenylene) and $[Ru(tap)_3]^{2+}$ and $[Ru(bipy)_2(tap)]^{2+}$ (bipy = 2,2′-bipyridine, tap = 1,4,5,8-tetraazaphenanthrene) for comparison purposes, have been examined. Hydroquinone (H_2quin) was chosen as the reductant for the photochemical reduction. Laser flash photolysis of these complexes with H_2quin led to two transients. It is shown, on the basis of the spectroelectrochemical reduction of free tap and hat and the corresponding complexes, that the first transient at ≈500 nm corresponds to the monoreduced complexes $[\{Ru(phen)_2\}_2(hat^{\bullet -})]^{3+}$, $[Ru(tap)_2(tap^{\bullet -})]^{+}$ and $[Ru(bipy)_2(tap^{\bullet -})]^{+}$ respectively; this is confirmed by the kinetic behaviour of their decays in the presence of oxidants such as benzoquinone (bquin) and O_2. The second transient at ≈350–400 nm has a much longer lifetime and is attributed to the semiquinone Hquin$^{\bullet}$, formed from the reduction of bquin (purposely added or present as traces of oxidant in the medium) by the photogenerated reduced complex. For the bimetallic complex an alternative pathway is proposed for the observation of the second transient.

It has been shown that ruthenium(II) complexes with 1,4,5,8-tetraazaphenanthrene (tap) and 1,4,5,8,9,12-hexaazatriphenylene (hat) interact with double-stranded DNA,[1–3] and behave as very powerful oxidizing agents in their ^{3}m.l.c.t. (metal-to-ligand charge transfer) excited states.[4,5] These excited complexes can therefore abstract electrons from the guanine bases of DNA. The so-formed radical cations of the guanine produce, after several subsequent processes, breaks in the strands of the polynucleotide.[6] More recently it has been shown that in competition with these cleavages, the primary photoelectron transfer also induces the formation of an adduct between the oxidized nucleic base and the monoreduced complex.[7] These tap and hat ruthenium(II) complexes are thus interesting photosensitizers of DNA reactions.

For these photosensitization studies, the best test to demonstrate the existence of a photoelectron transfer process from the DNA double helix to the excited complex consists in detecting the production of the transient monoreduced complex. This species thus needs to be clearly characterized both spectroscopically and kinetically. This is possible by studying the monoreduced complex produced in a simpler system than DNA, for example in the presence of a reductant such as hydroquinone, or in a spectroelectrochemical cell.

Thus the spectroelectrochemistry and flash photolysis in the presence of hydroquinone of the bimetallic complex $[\{Ru(phen)_2\}_2(hat)]^{4+}$ **I** (phen = 1,10-phenanthroline), and of monometallic compounds such as $[Ru(tap)_3]^{2+}$ and $[Ru(bipy)_2(tap)]^{2+}$ (bipy = 2,2′-bipyridine) for comparison purposes, have been examined in this work. The compound $[Ru(bipy)_2(tap)]^{2+}$, in addition to $[Ru(tap)_3]^{2+}$, was chosen because its acid–base properties in the ground and excited states are closer to those of the bimetallic compound.[4b]

The photochemical behaviour of the system '$[Ru(tap)_3]^{2+}$ + hydroquinone (H_2quin)' was examined several years ago in our laboratory.[8] On laser flash photolysis of $[Ru(tap)_3]^{2+}$ in the presence of H_2quin one transient, which corresponds to the monoreduced complex $[Ru(tap)_2(tap^{\bullet -})]^{+}$ (or $[Ru(tap)_3]^{+}$ in abbreviation), is observed [equation (1)]. The monoreduced species $[Ru(tap)_3]^{+}$ formed by quenching of the excited state by H_2quin [equation (1)] is reoxidized by the semiquinone Hquin$^{\bullet}$



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$$[Ru(tap)_3]^{2+*} + H_2quin \xrightarrow{k_q} [Ru(tap)_3]^{+} + Hquin^{\bullet} + H^{+} \quad (1)$$

(resulting from the loss of one electron and one proton from hydroquinone) according to a bimolecular equimolecular process [equation (2)] in a *degassed* solution. If the hydroquinone is

$$[Ru(tap)_3]^{+} + Hquin^{\bullet} + H^{+} \xrightarrow{k_{2ox}} [Ru(tap)_3]^{2+} + H_2quin \quad (2)$$

not added under vacuum to the degassed complex solution, traces of *p*-benzoquinone (bquin) are formed from oxidation of H_2quin.[8] As bquin can compete with Hquin• for the reoxidation of $[Ru(tap)_3]^+$ [equation (3)], this interferes with the second-

$$[Ru(tap)_3]^+ + bquin + H^+ \xrightarrow{k_{ps}[bquin]} [Ru(tap)_3]^{2+} + Hquin^{\bullet} \quad (3)$$

order process (k_{2ox}) so that the decay of $[Ru(tap)_3]^+$ is neither first nor second order. If an excess of bquin is added purposely to the medium, then $[Ru(tap)_3]^+$ is reoxidized according to a pseudomonomolecular process (k_{ps}[bquin]) and the corresponding lifetime of the monoreduced complex is given by $1/(k_{ps}$[bquin]).[8]

It should be noted that as the driving force for the photoelectron transfer from the excited complex to bquin is much lower than for the reductive quenching by H_2quin (a difference of 0.8 eV) no oxidative quenching of the excited complex by bquin occurs at least for [bquin] $\leqslant$ 1 mmol dm^{-3}.[8] Due to the highly oxidizing character of the tap and hat complexes, this remains true for the other complexes examined in this work.

Experimental

The homoleptic $[Ru(tap)_3]^{2+}$ and heteroleptic $[Ru(bipy)_2(tap)]^{2+}$ complexes were prepared according to published procedures.[4,9] The bimetallic complex $[\{Ru(phen)_2\}_2(hat)]^{4+}$ was also prepared as described previously.[5] Compounds Na_2HPO_4 and NaH_2PO_4 (Merck) were used to prepare the buffered solutions.

Laser Flash Photolysis.—The samples were excited at 355 nm with a neodinium YAG laser (Continuum NY 61–10), and the resulting transient absorptions recorded with an Applied Photophysics system, according to a procedure already described.[10] The solutions were deoxygenated by bubbling with argon for at least 30 min prior to each experiment. The concentration of hydroquinone (H_2quin) was such that a sufficient quenching percentage could be obtained. Hydroquinone was not added to the complex solution under vacuum, but to an argon purged solution; this procedure did not prevent the formation of *p*-benzoquinone in the hydroquinone solution.[8] The pH was adjusted to 7 with a 0.1 mol dm^{-3} phosphate buffer.

Electrochemistry and Spectroelectrochemistry.—Cyclic voltammetry was performed on a platinum disc electrode (approximate area = 20 mm^2) with dried and freshly distilled acetonitrile containing tetrabutylammonium hexafluorophosphate (Fluka) as supporting electrolyte; for the aqueous solutions [Milli-Q distilled water (Millipore)], a glassy carbon disc electrode (approximate area = 30 mm^2) was used with lithium nitrate (Fluka) as supporting electrolyte. The counter electrode was a large platinum grid. The potential of the working electrode was scanned between 0 and −2 V *vs* a saturated calomel electrode (SCE) and controlled by a home-made potentiostat (Radiometer K 701) separated by a Tacussel bridge from the acetonitrile solution.

The design and assembly of the spectroelectrochemical cell followed the previous literature.[11] The spectroelectrochemical cell was made of two 2 × 2 cm glass windows separated by a parafilm spacer. The two glass windows were pressed and sandwiched between two Teflon holders. The working electrode was an optically transparent gold minigrid (Buckbee Mears, St Paul, MN), 1000 wires per inch, 60% transmittance. The reference electrode was made of a AgCl coated silver foil which was prepared by applying 6 V (Philips PE 1227) between the silver foil and a platinum grid, both electrodes being immersed in a 0.1 mol dm^{-3} HCl solution. The counter electrode was a platinum foil. The aqueous and acetonitrile solutions were deoxygenated by bubbling with argon for at least 30 min and injected into the cell by a hypodermic needle. The supporting electrolytes were the same as for the cyclic voltammetry. The spectrum of the non-electrolysed compound was recorded first with a diode array spectrophotometer (HP 8452A); then the spectra of the compound in its first reduction wave (determined by cyclic voltammetry) were recorded after different reduction times with a home-made potentiostat.

Results

Spectroelectrochemistry.—In order to detect easily the monoreduced complex photoproduced after the laser pulse with a reducing agent, the complexes and free ligands were reduced electrochemically at a gold minigrid electrode and characterized by their visible absorption.

The potentials of the two first reduction waves determined by cyclic voltammetry in acetonitrile for the free ligands tap and hat and for the bi- and mono-metallic compounds are given in Table 1. As the reduction potential of the bimetallic complex in acetonitrile was not that negative, this potential was measured in water. This permitted a better comparison with the flash photolysis results of buffered solutions.

For free tap and hat the evolution of the absorption as a function of the reduction time is shown in Figs. 1 and 2 respectively. For tap a band at 590 nm is produced first, with a shoulder at ≈440 nm (spectra 1–6, Fig. 1). Further electrolysis induces another increase in absorption around 460 nm while the absorption at 590 nm decreases (spectra 6–10, Fig. 1). Thus the shoulder at 440 nm is progressively replaced by an increasing absorption at 460 nm. The 590 nm band would correspond to π–π* transitions of tap$^{\bullet -}$. The 460 nm band, probably formed from the first product, could correspond to the bireduced ligand produced by dismutation of the monoreduced tap$^{\bullet -}$. Both compounds (mono- and bi-reduced tap) are reoxidized at 0 V *vs.* SCE; however, the reoxidation is not totally reversible for the species absorbing at 460 nm. The features characterizing the electrochemical reduction of bipy in tetrahydrofuran[16a] are very similar to those of tap; the absorption of bipy$^{\bullet -}$ occurs[16] between 500 and 600 nm with a shoulder at ≈430 nm, and bipy^{2-} exhibits a band with a maximum at ≈430 nm.[16a]

On electrochemical reduction of hat (Fig. 2), a band with two maxima (410 and 440 nm) increases as a function of the polarization time, and disappears upon reoxidation at 0 V *vs.* SCE. There might be another absorption around 600 nm, but because of the very low solubility of hat in acetonitrile no better data could be obtained. For longer periods of electrolysis, the dismutation of the monoreduced ligand cannot be detected

Table 1 Electrochemical data for free tap and hat and for $[Ru(tap)_3]^{2+}$ and $[\{Ru(phen)_2\}_2(hat)]^{4+}$; platinum working electrode, supporting electrolyte 0.1 mol dm^{-3} NBu_4PF_6 in acetonitrile

Compound	$E_{red}{}^{1\,a}$/ V *vs.* SCE	$E_{red}{}^{2\,a}$/ V *vs.* SCE	Δ*E*/V
tap	−1.58	−2.10	≈0.52
hat	−1.42	−1.72	≈0.30
$[Ru(tap)_3]^{2+}$	−0.75	−0.89	≈0.14
$[\{Ru(phen)_2\}_2(hat)]^{4+}$	−0.49 −0.64[b]	−1.06	≈0.57

The remaining traces of oxygen are reduced at the potentials applied to the gold minigrid electrode (reduction of oxygen: −0.78 V *vs.* SCE in acetonitrile[12] and −0.51 V *vs.* SCE in water[13] for pH values above 4.5[14]). As the $O_2{}^{\bullet -}$ absorption appears below 340 nm[15] it does not disturb the detection of the visible bands associated with the monoreduced complex.

[a] The first and second reduction wave potentials $E_{red}{}^1$ and $E_{red}{}^2$ were determined by cyclic voltammetry ($\Delta E = E_{red}{}^2 - E_{red}{}^1$). [b] Glassy carbon electrode, supporting electrolyte 0.1 mol dm^{-3} $LiNO_3$ in water, pH 5.9.

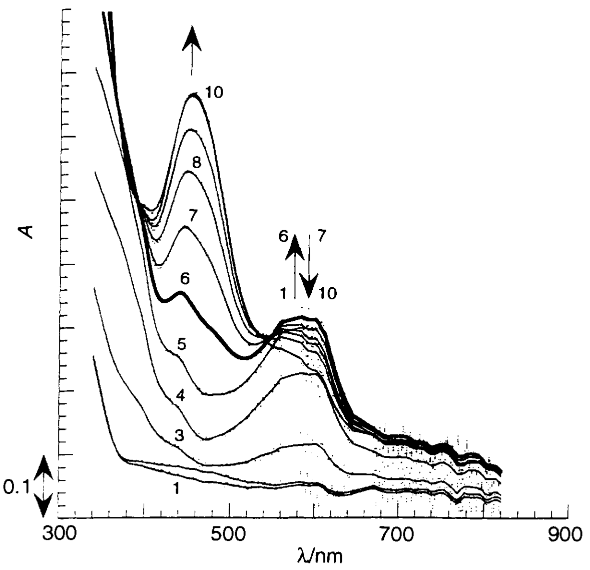

Fig. 1 Spectroelectrochemistry of tap 6 mmol dm^{-3} in acetonitrile at a gold minigrid electrode at a potential corresponding to the first reduction wave. Each spectrum was recorded after 3 min of polarization. Supporting electrolyte 0.1 mol dm^{-3} NBu_4Pt_6

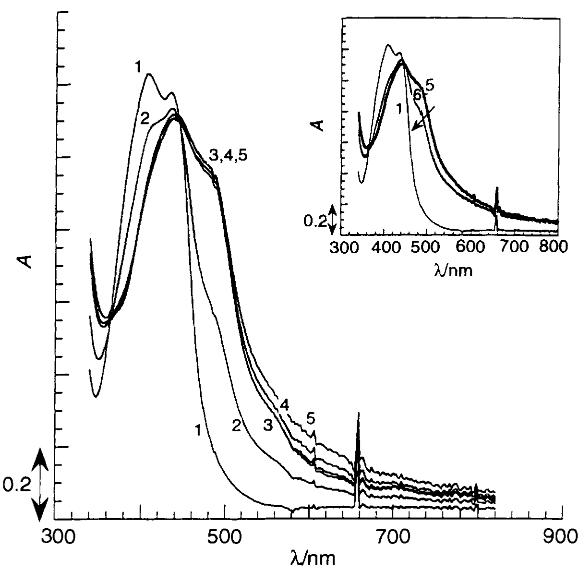

Fig. 3 Spectroelectrochemistry of $[Ru(tap)_3]^{2+}$ 2.4 mmol dm^{-3} in acetonitrile at a gold minigrid electrode at a potential corresponding to the first reduction wave. Each spectrum was recorded after 2 min of polarization. No important evolution is observed after the third spectrum (after 4 min). Supporting electrolyte 0.1 mol dm^{-3} NBu_4PF_6. Insert: after spectrum 5, reoxidation at 0 V *vs.* SCE produces spectrum 6 which differs from that of the starting material (spectrum 1)

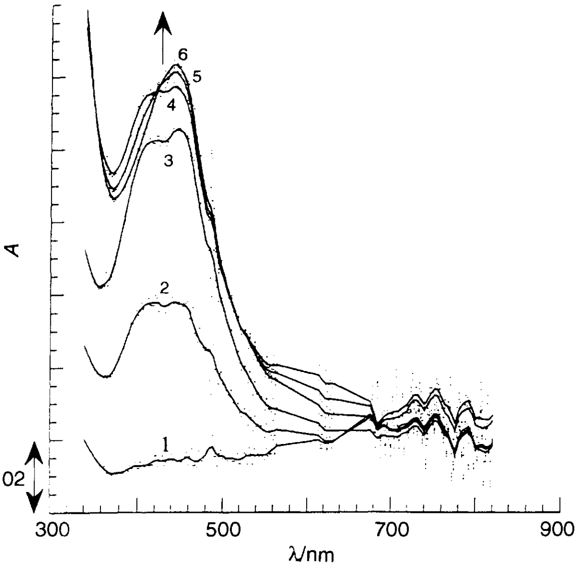

Fig. 2 Spectroelectrochemistry of hat 0.1 mmol dm^{-3} in acetonitrile at a gold minigrid electrode at a potential corresponding to the first reduction wave. Each spectrum was recorded after 2 min of polarization. Supporting electrolyte 0.1 mol dm^{-3} NBu_4PF_6

clearly; it seems however that the two absorption maxima transform into one maximum at ≈430 nm (Fig. 2, spectra 5 and 6), which could correspond to the dismutation of two hat$^{\bullet -}$ into hat^{2-} and hat. Another possibility would be that the weak absorption at ≈600 nm corresponds to hat$^{\bullet -}$ and the band at 440 nm to hat^{2-}. In that case spectrum 6 would originate from some decomposition product. Indeed, the reoxidation of the compound corresponding to spectrum 6, at 0 V *vs.* SCE is not complete.

The evolution of the absorption spectra of $[Ru(tap)_3]^{2+}$ after electrolysis is shown in Fig. 3. If a reversed bias (0 V *vs.* SCE) is applied after short electrolysis periods (2 min), 100% recovery of the starting absorption is observed. By contrast, if the reversed bias is applied after a longer time the reoxidation is not complete (insert of Fig. 3), which indicates some decomposition of the reduced complex, probably by loss of a ligand, in accordance with the occurrence of an absorption around 490–500 nm where complexes such as $[Ru(tap)_2X_2]$ ($X = Cl^-$ for example) absorb. This irreversibility had already been observed[8] from photoreduction of the complex by an irreversible reductant such as triethanolamine. For short periods of electrolysis, the appearance of absorption between 500 and 600 nm is in accord with the occurrence of π–π^* transitions typical of tap$^{\bullet -}$ (*cf.* Fig. 1). There is of course no complete disappearance of the m.l.c.t. absorption as the monoreduced complex still contains unchanged tap ligands responsible for the remaining m.l.c.t. transitions. Moreover the persistence of m.l.c.t. bands is also due to contamination by 'dechelated' complexes.

On electrochemical reduction of $[\{Ru(phen)_2\}_2(hat)]^{4+}$ (Fig. 4) absorption increases at ≈450 nm, where a minimum was present for the starting material, and where a product of reduction of hat absorbs (*cf.* Fig. 2), while the absorption at 570 nm, responsible for the lowest m.l.c.t. transition 'Ru–bridging hat' of the starting complex, vanishes. These observations are in accordance with the formation of the monoreduced species. Indeed, on reduction, an electron is added to the central bridging hat[17] and the resulting species should correspond to $[\{Ru(phen)_2\}_2(hat^{\bullet -})]^{3+}$ for which the m.l.c.t. transition from the metal to the bridging hat has disappeared as the accepting lowest π^* orbital has become occupied by the supplementary electron; this is accompanied by the occurrence of new π–π^* transitions centred on hat$^{\bullet -}$ (the other m.l.c.t. transitions to the other ligands remain). Reoxidation at 0 V *vs.* SCE regenerates 100% of the starting material at least during the electrolysis time which has been investigated.

Laser Flash Photolysis of the Bimetallic Complex $[\{Ru(phen)_2\}_2(hat)]^{4+}$.—*In the presence of hydroquinone.* The differential transient absorption of $[\{Ru(phen)_2\}_2(hat)]^{4+}$ in water, recorded 50 ns after the laser pulse and its ground-state absorption spectrum are shown in Fig. 5. The transient absorption corresponds mainly to the depletion of the starting complex, with a recovery time of 290 ns (≈10% error), in accordance with the value measured for the luminescence lifetime of the complex in water, *i.e.* 260 ns (≈3% error) (Table

Table 2 Emission maxima, luminescence lifetimes and quenching rate constants by hydroquinone in water

Compound	λ_{max}^{em}/nm	$\tau_{H_2O}^{(Ar)}$/ns	$\tau_{H_2O}^{(air)b}$/ns	$10^{-9}k_q^{c}$/dm^3 mol^{-1} s^{-1}
$[\{Ru(phen)_2\}_2(hat)]^{4+}$	800[a]	260	260	2.3
$[Ru(tap)_3]^{2+}$	602[d]	220	210	4.5
$[Ru(bipy)_2(tap)]^{2+}$	714[d]	145	140	0.7

[a] Uncorrected. [b] For a complete study of the oxygen effect in acetonitrile see ref. 18. [c] Obtained from Stern–Volmer plots of luminescence lifetimes measurements. [d] Ref. 9, corrected for the phototube response.

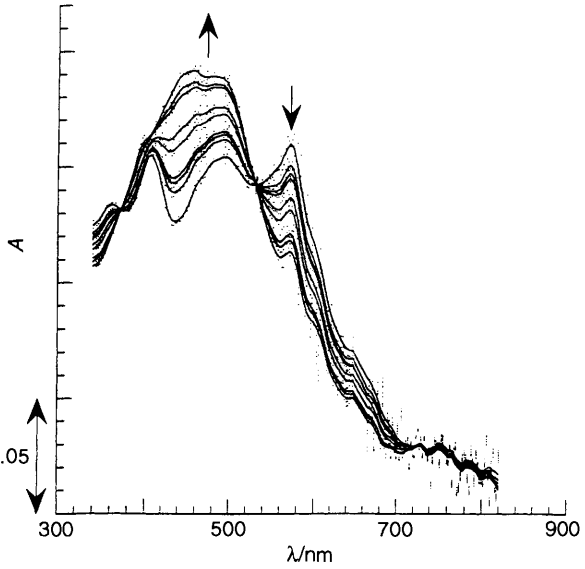

Fig. 4 Spectroelectrochemistry of $[\{Ru(phen)_2\}_2(hat)]^{4+}$ 0.3 mmol dm^{-3} in water, pH 5.9, at a gold minigrid electrode at a potential corresponding to the first reduction wave. Each spectrum was recorded after 2 min of polarization. Supporting electrolyte 0.1 mol dm^{-3} $LiNO_3$

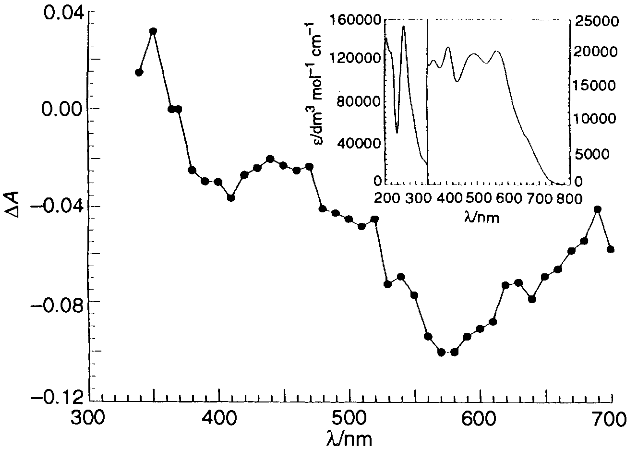

Fig. 5 Differential transient absorption recorded 50 ns after the laser pulse, for $[\{Ru(phen)_2\}_2(hat)]^{4+}$ in water, argon purged solution. Insert: absorption spectrum of $[\{Ru(phen)_2\}_2(hat)]^{4+}$ in water

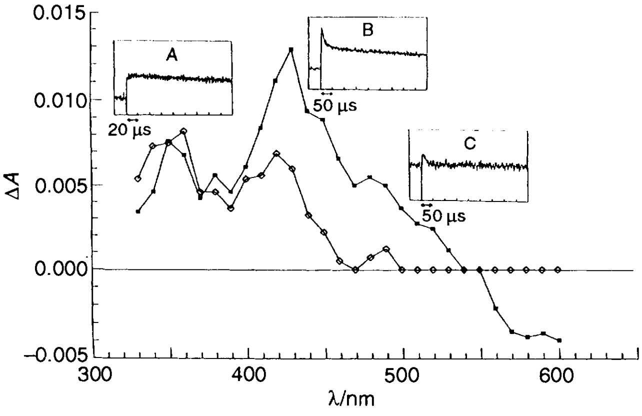

Fig. 6 Laser flash photolysis of $[\{Ru(phen)_2\}_2(hat)]^{4+}$ 5 × 10^{-5} mol dm^{-3} in water in the presence of 10^{-2} mol dm^{-3} H_2quin, argon purged solution. Differential absorption spectra recorded 2 µs (–■–) and 100 µs (–◇–) after the laser pulse. Decays of transient absorptions at 350 nm with 20 µs per division (insert A), at 430 nm with 50 µs per division (insert B), and at 500 nm with 50 µs per division (insert C)

2). The excited state of $[\{Ru(phen)_2\}_2(hat)]^{4+}$ starts absorbing at $\lambda < 450$ nm and is quenched by hydroquinone with a rate constant k_q of 2.3 × 10^9 dm^3 mol^{-1} s^{-1} as obtained from Stern–Volmer plots from measurements of luminescence lifetimes (Table 2). This value is a little lower than the quenching rate constant obtained previously[8] for $[Ru(tap)_3]^{2+}$ (4.5 × 10^9 dm^3 mol^{-1} s^{-1}) which is used in this study as a reference compound. In order to maximise the quenching of the excited binuclear complex by H_2quin a concentration of 10^{-2} mol dm^{-3} in H_2quin has been used (86% of quenching). With this concentration the results described below are the same in the presence or the absence of buffer (phosphate buffer, 0.1 mol dm^{-3} at pH 7).

Taking into account the oxidising power of the excited complex (+1.04 V *vs.* SCE[5]) and the reducing power of H_2quin in a neutral medium (+0.53 V *vs.* SCE[19]), the driving force for the photoelectron transfer process should be sufficient to produce the monoreduced bimetallic complex after the laser pulse. Experimentally, in the presence of H_2quin, two transients are detected from the transient differential absorptions recorded 2 and 100 µs after the laser pulse (Fig. 6). The absorption at 500 nm has completely disappeared while an absorption is still present at 430 nm where a double decay is observed (Fig. 6, insert B). The shorter decay lasts 20–25 µs and can be related to the decay observed at 500 nm which returns to the base line within 25 µs (Fig. 6, insert C). Unfortunately the very weak absorption at 500 nm excludes the possibility of a kinetic analysis at that wavelength; this is probably caused by the overlapping of the absorption of the transient and of the bleaching of the starting material. The second decay at 430 nm is characterized by a much longer decay time (> 2 ms, neither a mono- nor a bi-molecular decay, not shown). At 350 nm, the longer transient can also be observed (> 2 ms); similarly, its decay corresponds neither to a first nor to a second order, and it is preceded by a slight rise of absorption that lasts ≈20 µs (Fig. 6, insert A). In conclusion (see also Table 3), at 500 and 430 nm a transient disappears within 25 µs whereas simultaneously within 20–25 µs, another transient appears at 350 nm; the latter also absorbs at 430 nm and is characterized by a much longer decay time (> 2 ms).

The variation of experimental parameters such as the addition of oxidant (benzoquinone or oxygen) influences the decay and provides complementary data for the elucidation of the mechanism. This is developed below.

In the presence of hydroquinone and benzoquinone. In order to assign the reduced complex to one of the two observed transients, an excess of an oxidant, in this case benzoquinone, was added to the medium. The decay can be transformed into a pseudo-first-order process from which the lifetime of the transient can be determined. Under such conditions, as outlined in the introduction for $[Ru(tap)_3]^{2+}$, the monoreduced bimetallic species generated by photoreduction with H_2quin should also be reoxidized according to a pseudo-first-order process [equation (4); $k_{ps}[bquin]$ in s^{-1}].

$$\underset{\text{(monoreduced)}}{[\{Ru(phen)_2\}_2(hat^{\bullet -})]^{3+}} + \text{bquin(excess)} + H^+ \xrightarrow{k_{ps}[bquin]} [\{Ru(phen)_2\}_2(hat)]^{4+} + Hquin^{\bullet} \quad (4)$$

Laser flash photolysis under these conditions (presence of 10 mmol dm^{-3} H_2quin and 1 mmol dm^{-3} bquin) produces transient absorptions comparable to those of Fig. 6, but for which the decays (Fig. 7) are affected by the addition of bquin. At 430 nm the first decay is no longer observed [Fig. 7(*a*)]; in contrast a slight rise of the signal appears [Fig. 7(*b*)] in the 500 ns time-scale. On the other hand, the longer transient at 430 nm [Fig. 7(*a*)] has become shorter than without bquin and, interestingly, it can be analysed according to a first-order process, leading to a lifetime of 2 ms (Table 3). Such a long transient could not correspond to the monoreduced bimetallic complex although a first-order decay is obtained (see later). At 500 nm, where only the shorter transient absorbs, the addition of 1 mmol dm^{-3} bquin shortens the decay further from 25 µs (Fig. 6) to ≈250 ns [Fig. 7(*c*)]; however its intensity is too weak to test the order. This decay time at 500 nm corresponds approximately to the time needed for the second transient at 350 or 430 nm to appear [Figs. 7(*d*) and 7(*b*)], suggesting again that the second transient [2 ms at 430 nm in the presence of 1 mmol dm^{-3} bquin, Fig. 7(*a*)] could be formed from the first species absorbing at 500 nm.

The oxidative quenching of the excited complex by bquin can be neglected (a few %), due to the very poor reducing power of the excited binuclear species.

Oxygen effect. The effect of oxygen on the kinetic behaviour of the transients of Fig. 6 (observed with an argon purged solution) is in accord with a rapid reoxidation of the photogenerated reduced species by oxygen. Indeed at 430 nm, where two decays were detected in the absence of oxidant (Fig. 6, insert B), in the presence of oxygen (not shown) the first transient becomes too short to be observed on the same time-scale, so that only the longer signal is detected and corresponds neither to a first- nor a second-order process.

It should be noted that the luminescence lifetime of the complex is insensitive to the presence of oxygen in water (Table 2).

Table 3 Effect of the addition of bquin on the decays of the two transients observed by laser flash photolysis of $[\{Ru(phen)_2\}_2(hat)]^{4+}$, $[Ru(tap)_3]^{2+}$ and $[Ru(bipy)_2(tap)]^{2+}$ in the presence of H_2quin

Complex	λ/nm	$+H_2quin$	$+H_2quin$ + bquin
$[\{Ru(phen)_2\}_2(hat)]^{4+}$	430	>2 ms	2 ms (first order)
	500	≈25 µs	<500 ns
$[Ru(tap)_3]^{2+}$	360	>200 µs	≈120 µs
	520	≈40 µs	17 µs (first order)
$[Ru(bipy)_2(tap)]^{2+}$	390	≈500 µs	≈300 µs
	530	≈50 µs	15 µs (first order)

Hydroquinone concentration: 10^{-2} mol dm^{-3} for $[\{Ru(phen)_2\}_2(hat)]^{4+}$ and $[Ru(tap)_3]^{2+}$, 3×10^{-2} mol dm^{-3} for $[Ru(bipy)_2(tap)]^{2+}$. Concentration of bquin is 1 mmol dm^{-3}, λ is the wavelength of the kinetic analysis. When the analyses correspond neither to a first- nor a second-order process, the 'decay times' are of course not true lifetimes; in contrast when they correspond to first-order processes, the 'decay times' correspond to true lifetimes.

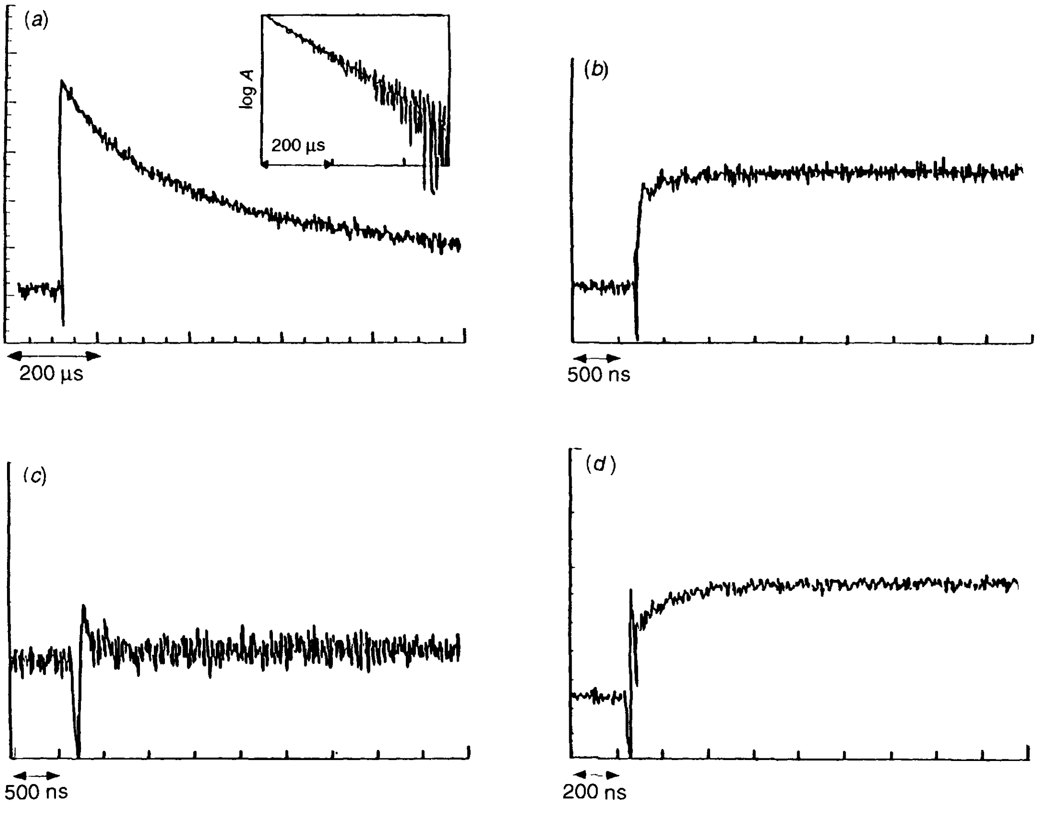

Fig. 7 Laser flash photolysis of $[\{Ru(phen)_2\}_2(hat)]^{4+}$ 5×10^{-5} mol dm^{-3} in water in the presence of 10 mmol dm^{-3} H_2quin *and* 1 mmol dm^{-3} bquin. Transient absorption monitored at: (*a*) 430 nm with a first-order decay (insert), time-scale 200 µs per division; (*b*) at 430 nm, time-scale 500 ns per division; (*c*) at 500 nm, time-scale 500 ns per division; (*d*) at 350 nm, time-scale 200 ns per division.

In order to clarify the kinetic behaviour of the bimetallic complex, by comparison with other Ru^{II} complexes, we have extended the flash photolysis study in the presence of hydroquinone to monometallic compounds such as $[Ru(tap)_3]^{2+}$ and $[Ru(bipy)_2(tap)]^{2+}$. As the absorption of these monometallic complexes is more hypsochromic[5] than that of the bimetallic compound, the detection at 500 nm of the monoreduced species should be easier. Indeed for $[Ru(tap)_3]^{2+}$ examined previously,[6] the monoreduced $[Ru(tap)_3]^+$ absorbs in the 490–500 nm region where the starting complex does not absorb. Although that study was carried out a few years ago, we have included complementary $[Ru(tap)_3]^{2+}$ results in the present work because no analyses were performed at wavelengths < 460 nm.*

Laser Flash Photolysis of Monometallic Ruthenium(II) *Complexes*.—$[Ru(tap)_3]^{2+}$ *in the presence of hydroquinone*. Re-examination of the flash photolysis of this system (see Table 2 for the luminescence lifetime and quenching rate constant by H_2quin) leads to the conclusion that two transient species are also produced, as evidenced by the differential transient absorption recorded 1 and 100 μs after the pulse (Fig. 8). As in the absorption spectrum obtained by spectroelectrochemistry for the reduced complex, a shoulder at > 500 nm is visible in the transient absorption after the laser pulse (Fig. 8) due to the absorption of $tap^{\bullet -}$ (*cf.* Fig. 1); the absorption from 500 nm down to 470 nm is due to the m.l.c.t. transition Ru–tap of the monoreduced complex $[Ru(tap)_2(tap^{\bullet -})]^+$. The fact that the absorbance is smaller in the 370–440 nm region originates from the depletion of the starting complex in this wavelength region. At 520 nm, where only the reduced complex absorbs, the duration of the decay is ≈40 μs (Fig. 8, insert B, Table 3) and corresponds neither to a first- nor a second-order process. In contrast in the presence of 1 mmol dm^{-3} bquin, the decay becomes first order with a corresponding lifetime of 17 μs (Fig. 8, insert C, Table 3).

Between 350 and 450 nm, where the second transient absorbs (Fig. 8), the decay time is ≈200 μs (Table 3) and becomes shorter (≈120 μs) in the presence of 1 mmol dm^{-3} bquin, but does not transform into a first-order process. At 380 nm (Fig. 8, insert A) a slight absorption rise appears during ≈40 μs in the absence of bquin and is shortened to ≈20 μs with 1 mmol dm^{-3} bquin; these times correspond to the decay times at 520 nm, again consistent with the formation of the second transient upon the disappearance of the reduced complex.

$[Ru(bipy)_2(tap)]^{2+}$ *in the presence of hydroquinone*. For this complex (see Table 2 for the luminescence lifetime and quenching rate constant by H_2quin) the results are similar to those with $[Ru(tap)_3]^{2+}$. The resulting differential transient absorption recorded 2 μs after the pulse (Fig. 9) is, however, different from that measured for $[Ru(tap)_3]^{2+}$, although in both cases the new bands which appear after photoreduction should originate from $tap^{\bullet -}$. This difference is due to the different ground-state absorption spectra of the two complexes[9] (Fig. 3), which generates a depletion in a different wavelength region.

At 350 nm in the absence of bquin (Fig. 9, insert A), the presence of two species can be detected as shown by the two decays (≈50 and ≈500 μs); both decay components are shortened by the addition of 1 mmol dm^{-3} bquin and by the presence of oxygen. The effect of 1 mmol dm^{-3} bquin on the transients at 390 and 530 nm is given in Table 3. At 410 nm, a rise in the absorbance during a time corresponding to the decay of the first transient is in accord with the production of the longer transient from the disappearance of the reduced complex (Fig. 9, insert B).

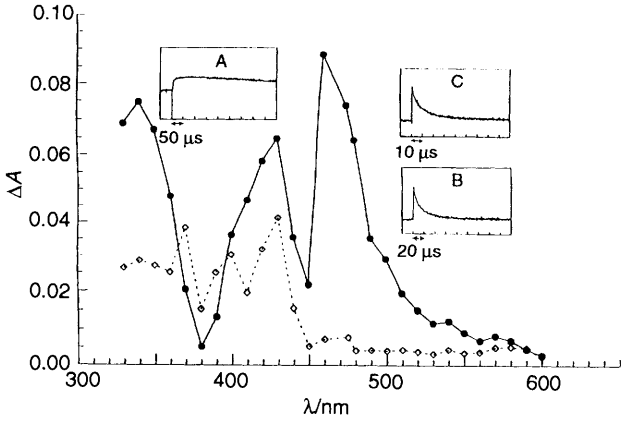

Fig. 8 Laser flash photolysis of $[Ru(tap)_3]^{2+}$ 10^{-4} mol dm^{-3} in water in the presence of 10^{-2} mol dm^{-3} H_2quin. Differential transient absorption recorded 1 μs (–●–) and 100 μs (---◇---) after the laser pulse. Decays at 380 nm (50 μs per division) for insert A, at 520 nm (20 μs per division) for insert B, and at 520 nm (10 μs per division) with 1 mmol dm^{-3} bquin for insert C

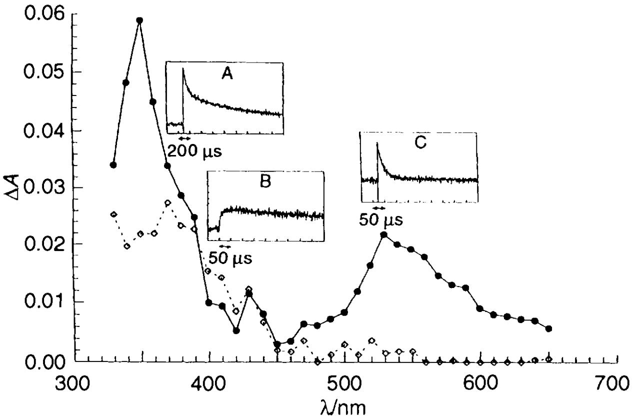

Fig. 9 Transient differential absorption for $[Ru(bipy)_2(tap)]^{2+}$ 1.2×10^{-4} mol dm^{-3} in water in the presence of 3×10^{-2} mol dm^{-3} H_2quin, 2 μs (–●–) and 60 μs (---◇---) after the laser pulse. Insert A: 350 nm, 200 μs per division; insert B: 410 nm, 50 μs per division; insert C: 530 nm, 50 μs per division

Discussion

The flash photolysis of the mono- and bi-metallic complexes shows clearly the formation of two transients absorbing in the regions of 500 and 350–450 nm; they can be identified on the basis of their kinetic behaviour and spectroelectrochemical data.

The Shorter Transient Species.—$[Ru(tap)_3]^{2+}$. The comparison of the spectra obtained by spectroelectrochemistry for the reduction of tap and $[Ru(tap)_3]^{2+}$, with the transient absorption obtained 1 μs after the laser pulse, is in accord with the assignment of the first transient to $[Ru(tap)_2(tap^{\bullet -})]^+$. Although the same absorption maxima are not found in the spectroelectrochemical spectra and in the transient absorption by flash photolysis, owing to the fact that, after the laser pulse, the spectrum corresponds to a differential absorption, the characteristics of $tap^{\bullet -}$ and of the Ru–tap m.l.c.t. transition are found in both cases. Moreover it is noteworthy that the transient absorption observed in the presence of H_2quin is similar to that recorded after the laser flash of $[Ru(tap)_3]^{2+}$ in the presence of another reductant such as guanosine 5′-monophosphate (GMP).[6] This constitutes additional confirmation of the assignment of the species in the 500 nm region to the monoreduced complex.

$[Ru(bipy)_2(tap)]^{2+}$. The same conclusion as above can be

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* The exciting beam was obtained with a pulsed nitrogen laser, Molectron UV 24, much less powerful (< 7 mJ) than the pulsed Continuum YAG laser used for this study (≈30 mJ at 355 nm).

drawn for $[Ru(bipy)_2(tap)]^{2+}$. The differential transient absorption detected 2 µs after the laser flash in the presence of H_2quin also shows an absorption in the 500–600 nm region, characteristic of $tap^{\bullet -}$ present in the monoreduced complex $[Ru(bipy)_2(tap^{\bullet -})]^{+}$.

$[\{Ru(phen)_2\}_2(hat)]^{4+}$. Comparison of the spectra of the electrochemically reduced $hat^{\bullet -}$ and $[\{Ru(phen)_2\}_2(hat^{\bullet -})]^{3+}$ with the differential transient absorption obtained by flash photolysis of the bimetallic compound in the presence of H_2quin (2 µs after the laser flash), indicates that the monoreduced species $[\{Ru(phen)_2\}_2(hat^{\bullet -})]^{3+}$ is produced after the laser pulse. Both species, the reduced hat and reduced bimetallic complex, shows a common intense band centred around 430–440 nm which is also present in the spectrum of the shorter transient (in the 450–500 nm region) and which is characteristic of $hat^{\bullet -}$ absorption.

bquin Effect. According to the kinetics of $[Ru(tap)_3]^{2+}$ examined previously,[8] the monoreduced complex should be reoxidized either by the semiquinone formed by photoelectron transfer [equation (2)] according to a bimolecular equimolecular process, or by traces of bquin (produced by oxidation of H_2quin in non-degassed solution). Consequently, in non-degassed solutions, and in the absence of added bquin, because of the competition between reactions (2) and (3) for the reoxidation of the monoreduced complex, the latter disappears according to neither a first- nor a second-order process (see Table 3 at 500, 520 or 530 nm for $[\{Ru(phen)_2\}_2(hat)]^{4+}$, $[Ru(tap)_3]^{2+}$ and $[Ru(bipy)_2(tap)]^{2+}$ respectively, where the transient absorption is not contaminated by the longer transient species).

In contrast, with an excess of bquin (1 mmol dm^{-3}), the monoreduced complex should be reoxidized according to a pseudomonomolecular reaction [equation (3)]. Table 3 shows that the addition of 1 mmol dm^{-3} bquin indeed transforms the decay of the shorter transient into a first-order process for $[Ru(tap)_3]^{2+}$ and $[Ru(bipy)_2(tap)]^{2+}$, leading to lifetimes of 17 and 15 µs respectively. For the bimetallic complex the weak intensity of the signal at 500 nm does not allow a reliable kinetic analysis; the bquin effect is, however, present (shortening of the time needed for the 500 nm transient to disappear). Although this observation is in agreement with the attribution of the short transient to the monoreduced bimetallic complex, the extremely short decay time (< 500 ns), compared to the 15–17 µs for the monoreduced monometallic complex is, however, intriguing. This is discussed below.

Oxygen effect. The monoreduced complex $[Ru(tap)_3]^{+}$ had also been shown previously to be oxygen sensitive.[6] Electron transfer from the monoreduced complex to oxygen is possible since the reduction potential of oxygen $[E_{red}(O_2/O_2^{\bullet -})]$ in water is −0.51 V *vs.* SCE (for pH values above 4.5; pK_a of the superoxide anion = 4.5[14]) and the oxidation potential of $[Ru(tap)_3]^{+}$ is −0.75 V *vs.* SCE.* The short transients for the bimetallic complex and the monometallic $[Ru(bipy)_2(tap)]^{2+}$ are also oxygen sensitive. This is in agreement with their assignment to the monoreduced complex as the oxidation potentials of $[\{Ru(phen)_2\}_2(hat^{\bullet -})]^{3+}$ (Table 1, −0.64 V *vs.* SCE in water) and $[Ru(bipy)_2(tap^{\bullet -})]^{+}$ (−0.88 V *vs.* SCE in MeCN) to the corresponding starting complexes are indeed negative enough to allow the reduction of oxygen.

The Longer Transient Species.—As mentioned above, the longer transient species appears when the monoreduced complex disappears in the absence or in the presence of purposely added bquin. Such behaviour would be compatible with the production of the semiquinone ($Hquin^{\bullet}$) from reaction (3), *i.e.* during the decay of the monoreduced complex by reoxidation by bquin (present as traces or purposely added). There are several arguments in favour of this hypothesis.

The spectroscopic data are in good agreement with production of $Hquin^{\bullet}$ by a route which follows the initial formation of $Hquin^{\bullet}$ during the laser pulse. The transient absorption, a few tens of µs (or 100 µs) after the laser pulse, *i.e.* when the monoreduced complex has disappeared by reaction (2) and/or (3), exhibits a maximum between 350 and 400 nm, where $Hquin^{\bullet}$ has been shown to absorb (λ_{max} of the acid form = 410 nm, λ_{max} of the basic form = 430 nm, pK_a = 4[19,20]). More $Hquin^{\bullet}$ should be produced during this second step when 1 mmol dm^{-3} bquin is added purposely to the solution, forcing the reoxidation of the monoreduced complex to take place by reaction (3) instead of (2). This is observed experimentally. For example in the case of the bimetallic complex, at 430 nm, where both the monoreduced complex and $Hquin^{\bullet}$ absorb, the decay of the reduced complex can be detected in the absence of 1 mmol dm^{-3} bquin (Fig. 6, insert B), whereas with 1 mmol dm^{-3} bquin at the same wavelength this decay is no longer observed [Fig. 7(*b*)] and instead a slight absorption rise is detected. This is due to the superposition of the weak decaying signal of the reduced species and of the more important rise of the $Hquin^{\bullet}$ signal [Fig. 7(*d*)] as $Hquin^{\bullet}$ is formed in a larger amount with 1 mmol dm^{-3} bquin by reaction (3) than when bquin is present as a contaminant in the medium.

Other kinetic arguments also favour $Hquin^{\bullet}$ as the second transient, at least for the monometallic complexes. The decays of the longer transient absorption at 360 or 390 nm for $[Ru(tap)_3]^{2+}$ or $[Ru(bipy)_2(tap)]^{2+}$ respectively (Table 3), do not correspond to first-order processes.† Moreover these non-monomolecular decays are kinetically sensitive to 1 mmol dm^{-3} bquin as would also be expected for $Hquin^{\bullet}$. Indeed with bquin, more $Hquin^{\bullet}$ transient should be formed by reaction (3) and therefore the time needed for the complete bimolecular decay of the signal becomes shorter (Table 3).

Although $Hquin^{\bullet}$ could be attributed to the long transient produced according to process (3), this hypothesis is, however, not fully compatible with all of the data on the bimetallic compound. Indeed, $Hquin^{\bullet}$ cannot disappear according to a first-order process,[21] whereas with $[\{Ru(phen)_2\}_2(hat)]^{4+}$ the disappearance of the longer transient at 430 nm (> 2 ms) becomes strictly first order in the presence of 1 mmol dm^{-3} bquin with a lifetime as long as 2 ms. These observations would suggest that a third species (*i.e.* in addition to the reduced complex and $Hquin^{\bullet}$) would be formed with the bimetallic system in the longer time domain, which should be sensitive to bquin. A possible candidate could be the bireduced binuclear complex originating from the dismutation of the monoreduced species. In accord with this possibility, it has been shown that the monoreduced, monoprotonated bipy and phen ligands,[22] as well as the monoreduced, monoprotonated complexes such as $[Ru(bpyz)_2(Hbpyz^{\bullet})]^{2+}$ and $[Ru(bipym)_2(Hbipym^{\bullet})]^{2+}$ (bpyz = 2,2′-bipyrazine, bipym = 2,2′-bipyrimidine)[23,24] can dismutate and generate the bireduced and the starting complexes. From these data, the bireduced complex should absorb hypsochromatically as compared to the starting material, which is indeed observed for the bimetallic system. Moreover as the bireduced, protonated compound should be less reductive than the monoreduced complex,[25] the bireduced species should be reoxidized more slowly by bquin than the monoreduced transient, which is compatible with the experimental results (decay of τ = 2 ms for the bimetallic complex and a few tens of µs for the monometallic compounds). It is not quite clear however why the monoreduced binuclear $[\{Ru(phen)_2\}_2(hat^{\bullet -})]^{3+}$ complex would dismutate whereas the corresponding monometallic compounds would not do so. An important

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* Value determined in acetonitrile.

† $Hquin^{\bullet}$ should disappear by dismutation according to a bimolecular process:[21] $2\ Hquin^{\bullet} \longrightarrow bquin + H_2quin$. However the decays are not strictly second order. Unsatisfactory bimolecular decays can be explained by non-homogeneous transient concentration within the path of the cell.

difference in behaviour between these two reduced complexes can however be found in the electrochemical data (Table 1). For the bimetallic complex[5] the second electron is added easily on the same central hat whereas for the monometallic compounds it is successively added to each ligand. It is also easier to add the second electron to the free hat than to the free tap (Table 1). These differences could be at the origin of the different photochemical behaviour. The attribution of the long transient (ms time-scale) to a bireduced complex would also be compatible with the spectroelectrochemical data of the hat ligand. Indeed it may be possible that in spectroelectrochemistry some absorption would be present at ≈500–600 nm which would correspond to hat$^{\bullet -}$ whereas the absorption at 400–450 nm (*i.e.* same absorption as the ms transient) would be due to hat^{2-}. Moreover, according to the dismutation hypothesis, the bireduced binuclear complex should originate from the disappearance of the monoreduced species, and therefore the production of the bireduced compound should diminish in the presence of 1 mmol dm^{-3} bquin, if the oxidation of the monoreduced complex by bquin is rapid enough to compete with its dismutation. Although bquin indeed has an effect on the decay time of the monoreduced bimetallic complex at 500 nm (Table 3), it does not seem that bquin diminishes the amount of bireduced compound as the 2 ms transient, *i.e.* the hypothetical bireduced complex, is still largely detected with 1 mmol dm^{-3} bquin.

No definitive conclusion can be drawn for the bimetallic complex, and the mechanism which is involved after the primary photoelectron transfer is thus rather complicated especially because of the superposition of absorption of several different species, among them the starting complex which absorbs in the whole spectral region analysed.

Conclusion

The photo-induced production of the monoreduced complex in the presence of H$_2$quin, for the mono- and bi-metallic complexes, has been clearly shown. The data will thus facilitate the detection of the same photoreduced transients produced in more complicated systems such as DNA. This is particularly important for the bimetallic complex $[\{Ru(phen)_2\}_2(hat)]^{4+}$ which has recently been shown to photoreact with DNA.[26] The long transient seems to correspond to Hquin$^{\bullet}$ produced in a second step, in excess compared to the amount of monoreduced complex, although the mechanism does not appear to be compatible with all the data on the bimetallic complex.

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