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Dependence of the photophysical and photochemical properties of the photosensitizer tris(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) on pH

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Abstract

The pH dependence of the photoluminescent properties and the emission quenching of tris(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) ($Ru(dhch)_3$) by ferricyanide ion ($Fe(CN)_6{}^{3-}$), methyl viologen (MV^{2+}), cupric ion (Cu^{2+}), *N*,*N*'-bis(3-sulphopropyl)-4,4'-bipyridinium inner salt ($V^{2+}(PS^-)_2$), nitrobenzene and O_2 were investigated. The emission intensity and excited state lifetime of the complex are at a minimum and the wavelength of the emission peak is at a maximum near pH 3. The solubility of the complex is at a minimum near pH 2. These results indicate that two carboxylic acid groups are present in the dissociated state near pH 2. The pK_a values of the conjugated acid of the two dissociated carboxylate groups were estimated from luminescence titration and excited state lifetime data to be 0.7 and 3.8 for the ground state and excited state of the complex respectively. The corresponding values for the four less acidic carboxylic acid groups are 3.7 and 8.2. The rate of quenching of $^*Ru(dhcb)_3$ by $Fe(CN)_6{}^{3-}$ is greater at lower pH, whereas the opposite trend is observed for reaction with the other quenchers. The rate of quenching by Cu^{2+} is unusually fast, presumably due to the chelation of Cu^{2+} to the carboxylate groups of the complex. The order of the oxidation potentials of the excited state Ru(II) complexes is $^*Ru(dhcb)_3{}^{2+} < {}^*Ru(dhcb)_3{}^{4-} < {}^*Ru(bpy)_3{}^{2+}$. This order is the same as that of the quenching rate constants for the complexes by neutral or zwitterionic quenchers.

Keywords: Photosensitizer; Ru(II) complex; Tris(4,4'-dicarboxy-2,2'-bipyridine)Ru(II); Quenching; Proton transfer

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1. Introduction

Tris(α,α'-diimine)ruthenium(II) complexes have attracted considerable attention as photosensitizers in photoenergy conversion [1] and luminescent probes for the characterization of microheterogeneous systems [2,3]. The photophysical and photochemical properties of the metal complexes are modified greatly on binding with microparticles such as micelles, polyelectrolytes and inorganic colloidal particles [2,3]. Most of the previous studies used neutral ligands giving cationic complexes. Thus, the investigation of microheterogeneous systems was limited to anionic species.

A few workers have reported the excited state properties of the Ru(II) complex $Ru(bpy)_2(dhcb)^{2+}$ containing mixed ligands of 2,2'-bipyridine (bpy) and 4,4'-dicarboxy-2,2'-bipyridine (2,2'-bipyridine-4,4'-dicarboxylic acid ($bpy(COOH)_2$), (dhcb). Giordano et al. [4] and Kaneko et al. [5] reported the acid dissociation constant for the metal-to-ligand charge transfer state of the complex. The pH dependences of the photophysical properties of the complex were also reported [5–7].

Tris(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) ($Ru(dhcb)_3$) (dhcb is used for the undissociated and dissociated ligand; when necessary, the charge of the complex is given) is a highly efficient photosensitizer for the photochemical splitting of water [8,9] and in photoelectrochemical cells [10–12]. The complex has been used as an extramicellar probe to monitor the association of cations with anionic micelles [13]. The charge of the Ru(II) complex can be changed from +2 to −4 and thus it may bind to both anionic and cationic microparticles, depending on the pH of the medium. In this paper, we report the acid–base equilibria of the ground and excited states and the pH dependence of the photophysical and photochemical properties of the metal complex in homogeneous aqueous and micellar media.

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2. Experimental details

2.1. Materials

$Ru(dhcb)_3$ was prepared by the modification of the method of Foreman et al. [13]. A 1 : 3.3 molar ratio of $RuCl_3$ (Aldrich) and 2,2′-bipyridine-4,4′-dicarboxylic acid (Aldrich) in dimethylformamide solution containing hydroxylamine was refluxed for 7 days under nitrogen. After removal of the solvent under reduced pressure, a small amount of water was added and the product was dissolved by adjusting the pH of the medium to pH 8 with 1.0 M NaOH. After filtering off the undissolved solid, the complex was precipitated by adjusting the pH of the filtrate to 2.7 with 1.0 M HCl. The dissolution and precipitation cycle was repeated until no further change in the absorption spectrum of the product was observed. Methyl viologen dichloride ($MV^{2+}2Cl^-$) and *N,N*′-bis(3-sulphopropyl)-4,4′-bipyridinium inner salt ($V^{2+}(PS^-)_2$) were obtained from Aldrich and used without further purification. Other chemicals were obtained from commercial sources and were of reagent grade. Water was deionized and distilled in acidic $KMnO_4$ using a glass apparatus.

2.2. Solubility measurements

About 20 mg of the metal complex was suspended in 10 ml of an appropriate aqueous medium (prepared by mixing 1.0 M HCl and 1.0 M sodium cacodylate) and stirred for 3 h at 25 °C. The solution was filtered through a thermostatically controlled glass filter. The pH of the filtrate was adjusted to pH 7 with 1 M NaOH and diluted appropriately with 0.1 M cacodylate buffer (pH 7). The concentration of the metal complex of the dilute solution was determined from the absorbance value at 464 nm using $\epsilon = 2.6 \times 10^4$ M^{-1} cm^{-1} [11].

2.3. Spectral measurements

The absorption spectra were taken on a Beckman DU-8B spectrophotometer. Luminescence spectra were recorded on a Hitachi F-3010 spectrofluorometer at 25 °C. Unless otherwise specified, the pH of the solution for recording of the luminescence spectrum was adjusted with 0.01 M cacodylate/0.09 M NaCl and 0.10 M HCl. The emission intensities were corrected for the variation in detector sensitivity with wavelength using rhodamine B and methylene blue [14]. The excitation wavelength was the isosbestic point of the metal complex (475 nm). Deaeration of the solution was achieved by bubbling water-saturated N_2 gas until no additional spectral change was observed by further bubbling (at least 30 min). The excited state lifetimes of the complex were obtained with a picosecond time-resolved single-photon-counting system assembled by Korea Standard Research Institute. Correction of the intensity of the incident light was made for quenching experiments using ferricyanide ion as quencher.

2.4. Cyclic voltammetry measurements

These were carried out using a BAS 100B electrochemical analyser. Solutions (1.0 mM) of $Ru(dhcb)_3$ were prepared in 2 M $HClO_4$ and 0.1 M $NaClO_4$ at pH 5.6. For $MV^{2+}2Cl^-$, $V^{2+}(PS^-)_2$ and $K_3Fe(CN)_6$, 1.0 mM solutions in 0.1 M KCl were used. All voltammograms were recorded under an N_2 atmosphere with a glassy carbon working electrode, a Pt wire auxiliary electrode and a saturated calomel electrode (SCE) as reference. Potentials are expressed relative to a normal hydrogen electrode (NHE) except in Fig. 6 (see later).

3. Results and discussion

We first describe the pH dependence of the spectral properties and solubility of $Ru(dhcb)_3$; this is discussed in terms of the acid–base equilibria of the ground and excited states of the complex. The results are confirmed by experiments with cationic and anionic micelles. We then present the results of the quenching experiments to support our arguments and explain these results in terms of the redox potentials of the species involved and other factors.

3.1. Dependence of the luminescence properties and solubility of $Ru(dhcb)_3$ on pH

The luminescence spectrum of $Ru(dhcb)_3$ is highly dependent on the pH of the medium (Fig. 1). The emission intensity is at a minimum near pH 3. The wavelength of the emission maximum decreases as the emission intensity increases (Fig. 2). Unlike other tris(2,2′-diimine)Ru(II) complexes of undissociated ligands, the emission decay profile of $Ru(dhcb)_3$ does not follow a single-exponential function. The decay shows a fast component followed by a slow component. The lifetime of the slow component is typical of Ru(II) complexes. The appearance of the fast component seems to be due to protonation–deprotonation of the excited complex (see below). In Table 1, we summarize the excited state lifetimes. The variation of the average excited state lifetime with pH is similar to that of the emission intensities.

The UV–visible absorption spectrum of the complex also varies with the pH of the solution (spectra not shown). However, the pH dependence of the absorption spectrum is much less pronounced than that of the luminescence spectrum: isosbestic points are observed at 430 and 475 nm in the pH range 3–7 and the

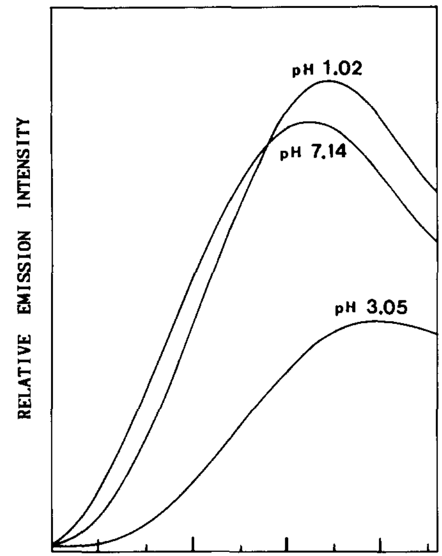

Fig. 1. Corrected luminescence spectra of 5.0×10^{-6} M $Ru(dhcb)_3{}^{2+}$ at three different pH values.

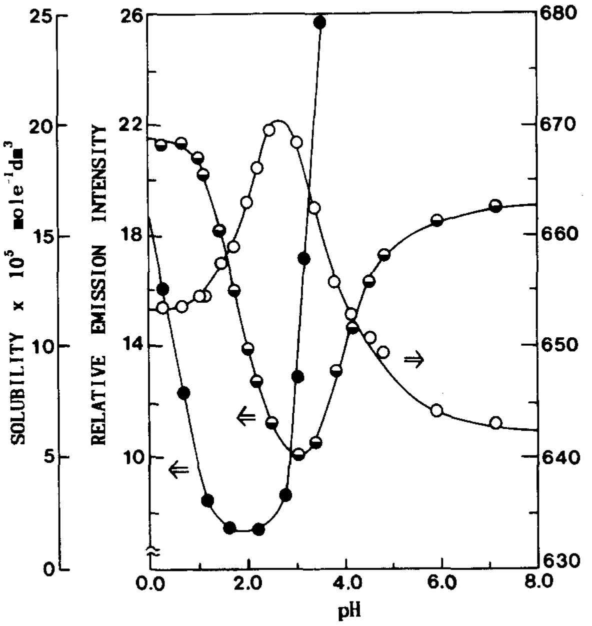

Fig. 2. The pH dependence of the peak emission intensity (◐), wavelength of the emission maximum (○) and solubility (●) of $Ru(dhcb)_3{}^{2+}$. The concentration of the complex for the emission spectra is 5.0×10^{-6} M. The excitation wavelength is 475 nm, an isosbestic point.

Table 1
Lifetime data of tris(4,4′-dicarboxy-2,2′-bipyridine)ruthenium(II) at 25 °C in air-saturated aqueous solutions[a]

Medium	τ_1 (ns) (A_1)	τ_2 (ns) (A_2)	$\langle\tau\rangle$ (ns)[d]
pH 0, water	1 (0.64)	524 (0.36)	522
pH 1, water[b]	1 (0.64)	502 (0.33)	492
pH 1, 10 mM CTAB[b]	1 (0.64)	504 (0.33)	494
pH 1, 10 mM SDS[c]	1 (0.62)	740 (0.34)	720
pH 1.5, water	1 (0.59)	467 (0.41)	466
pH 2.0, water	4 (0.31)	414 (0.69)	412
pH 3.0, water	13 (0.24)	326 (0.76)	322
pH 7.0, water	20 (0.07)	462 (0.93)	461
pH 7.0, 10 mM CTAB	0.8 (0.69)	516 (0.31)	514
pH 7.0, 10 mM SDS	18 (0.08)	465 (0.92)	464

[a] Fitted to $I(t)=A_1e^{-t/\tau_1}+A_2e^{-t/\tau_2}$.

[b] Better fit obtained with a third component of $\tau_3=125$ ns and $A_3=0.03$.

[c] Better fit obtained with a third component of $\tau_3=234$ ns and $A_3=0.04$.

[d] Average value calculated by $\langle\tau\rangle=(\Sigma_iA_i\tau_i^2)/(\Sigma_iA_i\tau_i)$.

maximum absorbance value (near 460 nm) is about 2% less at pH 7 than at pH 3. These observations match well the findings made for $Ru(bpy)_2(dhcb)$ [4].

The solubility of $Ru(dhcb)_3$ is at a minimum at pH 2 (1.7×10^{-5} mol dm^{-3}). (The reported limiting solubility of $Ru(dhcb)_3$ is $(3\pm1)\times10^{-6}$ mol dm^{-3} at pH 3 [9]. The discrepancy between this reported value and ours may be due to the different ionic strength of the medium (1.0 M in this work and no added salt in ref. 9). The observed increase in solubility on addition of ethylenediaminetetraacetic acid (EDTA) [9] may reflect this.) Either raising or lowering the pH of the solution from pH 2 increases the solubility of the complex (Fig. 2). Potentiometric titration of the suspension of $Ru(dhcb)_3$ which was recovered as a precipitate at pH 2.7 (in the absence of added salt) indicates that four equivalents of base are required to solubilize the complex and to bring the pH of the solution to pH 7. These results suggest that the precipitate is an inner salt and two carboxylate groups of the ligands of the precipitated complex remain in the deprotonated form. The bimodal dependence of the luminescence properties of the Ru(II) complex on pH provides further evidence for the presence of two types of carboxylate group which differ in their dissociation constants. The luminescence titration curve above pH 3 is similar to that of a monobasic acid, indicating that four COOH groups of a total of six are present as the protonated form in the inner salt and have approximately the same pK_a value $(pK_a)_1$. This is also supported by the observation of isosbestic points in the absorption spectrum (pH 3–7). The titration curve below pH 3 shows that the other two acid groups dissociated in the inner salt have the same pK_a value $(pK_a)_2$. Similarly, it has been reported that the pK_a values of two COOH groups of $Ru(bpy)_2(dhcb)$ are the same [4].

If we assume that only a zwitterion of net zero charge is present in the solution at pH 2 under the experimental conditions of the solubility measurements, the solubility of the complex at $pH=(pK_a)_2$ would be 16 times the minimum solubility (at pH 2). (The concentration of the species M_i, with i protons dissociated among n independent acidic groups, is given by $[M_i]=[M_0](n!)/\{i!(n-i)!\}\{k/[H^+]\}^i$, where k is the acid dissociation of the acidic groups [15].) Similarly, the solubility of the complex is four times the minimum solubility at pH = $(pK_a)_1$. The estimated pK_a values from the solubility titration curves are 3.7 and 0.7 respectively.

The emission intensity vs. pH profile is shifted to the higher pH region compared with the solubility vs. pH profile (Fig. 2). This is due to the excited state proton transfer equilibria of the complex. The inflexion points for the emission intensity are 1.8 and 4.2. If we assume that the excited state lifetimes of the fully protonated, zwitterionic and fully deprotonated forms of the complex are those measured at pH 0, 3 (where the emission intensity is at a minimum) and 7 respectively, the dissociation constants of the excited state complex (pK_a^*) are estimated from the relationship [4]: $2pH = pK_a^* - \log(\tau_{acid}/\tau_{base})$. The calculated pK_a^* values from the lifetime data in Table 1 are 3.8 and 8.2. The pK_a^* value for $^*Ru(dhcb)_3^0/^*Ru(dhcb)_3^{4-}$ is slightly higher than the corresponding value ($pK_a^* = 7.75$) [5] for $^*Ru(bpy)_2(dhcb)^{2+}/^*Ru(bpy)_2(dhcb)^0$, presumably due to electrostatic effects. The acid–base equilibria of the complex can be represented by Scheme 1.

$$\begin{tikzcd}
\mathrm{Ru(dhcb)_3^{2+}} \arrow[r, shift left, "(pK_a)_1 = 0.7"] \arrow[d, shift right, "h\nu"'] & \mathrm{Ru(dhcb)_3^{0}} \arrow[l, shift left] \arrow[r, shift left, "(pK_a)_2 = 3.7"] \arrow[d, shift right, "h\nu"'] & \mathrm{Ru(dhcb)_3^{4-}} \arrow[l, shift left] \arrow[d, shift right, "h\nu"'] \\
\mathrm{{}^*Ru(dhcb)_3^{2+}} \arrow[r, shift left, "(pK_a^*)_1 = 3.8"] \arrow[u, shift right, "\tau = 522\ \mathrm{ns}"'] & \mathrm{{}^*Ru(dhcb)_3^{0}} \arrow[l, shift left] \arrow[r, shift left, "(pK_a^*)_2 = 8.2"] \arrow[u, shift right, "\tau = 322\ \mathrm{ns}"'] & \mathrm{{}^*Ru(dhcb)_3^{4-}} \arrow[l, shift left] \arrow[u, shift right, "\tau = 461\ \mathrm{ns}"']
\end{tikzcd}$$

Scheme 1. The acid–base equilibria of ground and excited state $Ru(dhcb)_3$: ionic strength of the medium is 1.0 M for the ground state and 0.1 M for the excited state.

The addition of the anionic surfactant sodium dodecylsulphate (SDS) to a solution of $Ru(dhcb)_3$ at pH 1 or the cationic surfactant cetyltrimethylammonium bromide (CTAB) to a solution of the complex at pH 7 results in an increase in the emission intensity and a blue shift of the emission maximum by about 4 nm. The effects of the surfactants level off when their concentrations exceed 1 mM. Fig. 3 shows the results obtained with CTAB. The changes in the emission intensity on addition of the surfactants parallel the excited state lifetimes of the complex (Table 1). Also, the presence of 10 mM SDS shifts the inflexion point of the lower pH region of the emission intensity vs. pH profile to 2.5 from 1.8, whereas CTAB shifts the inflexion point of the higher pH region to 4.0 from 4.2. The presence of SDS does not affect the emission properties of the complex at pH > 3, and CTAB has no influence on the properties at pH < 3. These results indicate clearly that $Ru(dhcb)_3$ behaves as a cation below pH 3 and an anion above pH 3, and the metal complex binds to the oppositely charged micelle, but not to the micelle of the same charge. The shifts of the inflexion points in the presence of the ionic micelles are due to the change in pK_a^* values of the complex on binding to the micelles: binding of an acid to an anionic micelle results in a decrease in its pK_a value, while binding to a cationic micelle increases the pK_a value of the acid [16].

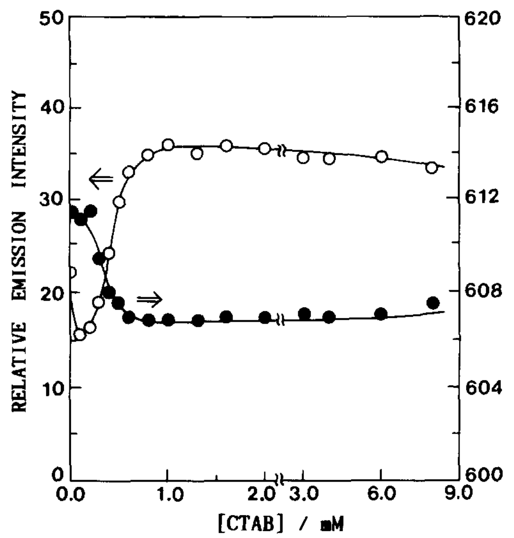

Fig. 3. Variation of the emission intensity (○) and emission maximum (●) of 5.0×10^{-6} M $Ru(dhcb)_3^{4-}$ in aqueous solutions at pH 7 with [CTAB].

The enhancement of the emission intensity of $Ru(dhcb)_3$ on addition of a micelle is in accord with the effect of anionic micelles on cationic Ru(II) complexes (RuL_3^{2+}) bearing neutral ligands [17]. However, the blue shift of the emission maximum by the micelles differs from the usual micellar effect on RuL_3^{2+}, which shows a red shift [17]. The overall changes in the emission properties of $Ru(dhcb)_3$ caused by the micelles are similar to those observed when RuL_3^{2+} binds to a rigid matrix or compact form of poly(methacrylic acid) [3,18]. This implies that the spectral changes of $Ru(dhcb)_3$ are largely due to the restricted rotational mobility of the ligand around the metal of the complex on binding to the ionic micelles.

3.2. *Quenching of $Ru(dhcb)_3$ luminescence by $Fe(CN)_6^{3-}$, MV^{2+}, $V^{2+}(PS^-)_2$, Cu^{2+}, O_2 and nitrobenzene*

The quenching of the luminescence of $Ru(dhcb)_3$ by ferricyanide ion ($Fe(CN)_6^{3-}$), 1,1′-dimethyl-4,4′-bipyridinium ion (dimethyl viologen, MV^{2+}), cupric ion (Cu^{2+}), *N*,*N*′-bis(3-sulphopropyl)-4,4′-bipyridinium inner salt ($V^{2+}(PS^-)_2$) and nitrobenzene was investigated at pH 1 (in 0.10 M HCl), 3.0 and 7.0. The Stern–Volmer plots for quenching in solutions at pH 1 and 7.0 are shown in Figs. 4 and 5 respectively. Except for the quenching by Cu^{2+} at pH 7, they show good linear relationships. The bimolecular quenching rate constants were calculated from the slopes of the plots (K_{SV}) and the excited state lifetimes (τ) given in Table 1 using

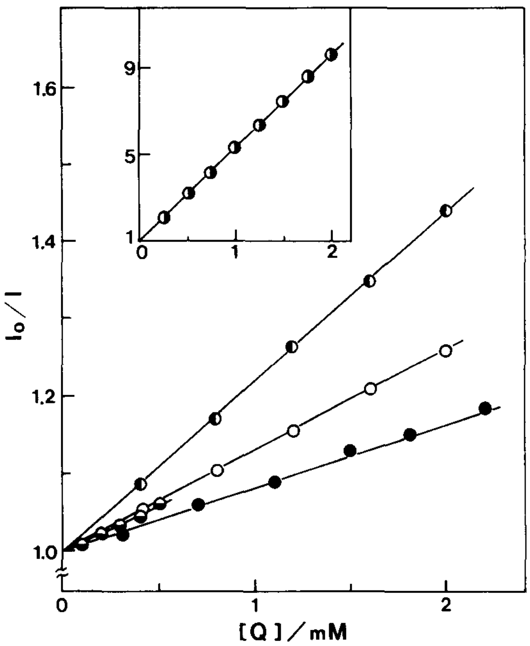

Fig. 4. Stern–Volmer plots for the emission quenching of $Ru(dhcb)_3$ in aqueous 0.1 M HCl solutions. Quenchers are nitrobenzene (●), Cu^{2+} (◒), methyl viologen (○), N,N′-bis(3-sulphopropyl)-4,4′-bipyridinium inner salt (◐) and $Fe(CN)_6^{3-}$ (◑).

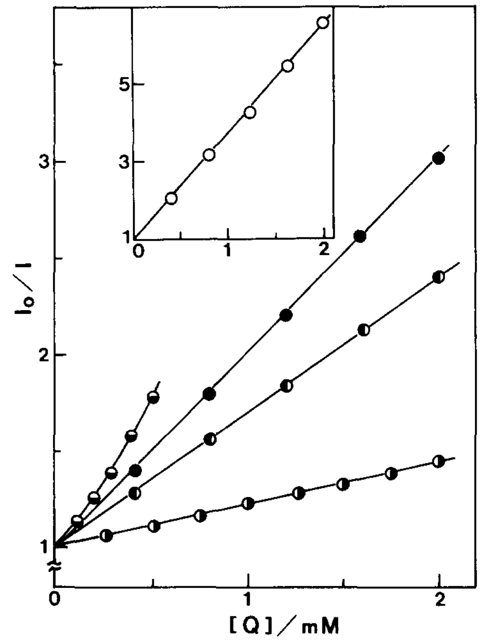

Fig. 5. Stern–Volmer plots for the emission quenching of $Ru(dhcb)_3$ in aqueous 0.1 M NaCl solutions at pH 7. Quenchers are nitrobenzene (●), Cu^{2+} (◒), methyl viologen (○), N,N′-bis(3-sulphopropyl)-4,4′-bipyridinium inner salt (◐) and $Fe(CN)_6^{3-}$ (◑).

the relationship $k_q = K_{SV}/\tau$. The results are shown in Table 2. For Cu^{2+} at pH 7, we took the quenching data at 0.30 mM Cu^{2+} and the k_q value was estimated. We also determined the rate constants for quenching by O_2 from the emission intensity data obtained from air-saturated and deaerated solutions using the concentration of O_2 in air-saturated 0.1 M NaCl solution as 2.48×10^{-4} M [3,19]. The result is included in Table 2, together with the rate constants for the emission quenching of $Ru(bpy)_3^{2+}$ for comparison.

From the electrostatic effect on the rate of reaction between charged species, the pH dependence of k_q for $Fe(CN)_6^{3-}$ and MV^{2+} is apparent: the quenching rate of $Ru(dhcb)_3$ by the anion $Fe(CN)_6^{3-}$ is fastest at pH 1 where the complex is present mainly in the dicationic form and slowest when the complex is in the tetra-anionic form (at pH 7); the rate for the cation MV^{2+} shows an opposite pH dependence. The presence of the cationic micelle CTAB at pH 7 accelerates the quenching reaction with $Fe(CN)_6^{3-}$, but retards that with MV^{2+}. These results can be attributed to the effect of local concentrations of reacting pairs on binding of the anionic species $Ru(dhcb)_3^{4-}$ and $Fe(CN)_6^{3-}$, but not the cationic species MV^{2+}, to the micelle. At pH 1, no significant effect of CTAB on the rate of reaction between $Ru(dhcb)_3$ and the cationic or neutral quenchers is observed. This indicates that $Ru(dhcb)_3$ is in the cationic form at this pH and does not bind to the micelle.

The quenching rate constants of $Ru(dhcb)_3$ by Cu^{2+} are similar to those obtained with MV^{2+}, which is in agreement with the report by Foreman et al. [13]. In contrast, the k_q value of $Ru(bpy)_3^{2+}$ with Cu^{2+} is one order of magnitude less than that with MV^{2+} (Table 2). The chelation of Cu^{2+} to the carboxylate groups of the ligands of $Ru(dhcb)_3$ may be responsible for the large quenching rate of $Ru(dhcb)_3$ by Cu^{2+}. Interestingly, the rates of the quenching reactions of $Ru(dhcb)_3$ by the zwitterion $V^{2+}(PS^-)_2$ and the neutral quenchers (nitrobenzene and O_2) depend on the pH. Such a pH dependence of the quenching rate is not observed with $Ru(bpy)_3^{2+}$. This indicates that, in addition to the electrostatic effect, other factors contribute to the pH dependence of the quenching rate of $Ru(dhcb)_3$.

The quenching reactions of Ru(II) complexes with the quenchers used in this study are known to be due to oxidative quenching (Eq. (1))

$$^*Ru(II) + Q \longrightarrow Ru(III) + Q^- \tag{1}$$

A possible exception is the quenching by O_2 [20]. In this case, the reaction rate depends on the oxidation potential of the excited electron donor *Ru(II) and the reduction potential of the electron acceptor, i.e. quencher Q [1c].

The reported redox potential for $^*Ru(bpy)_3^{2+/3+}$ is 0.84 V [21]. It has been shown that the redox potentials of other *Ru(II/III) couples bearing ligand (L) can be easily estimated from electrochemical and luminescence data by Eq. (2) [21]

$$E^{L}(^*2+/3+) = 0.84 - [E^{L}(2+/3+) - E^{bpy}(2+/3+)] - \Delta h\nu \ (V) \tag{2}$$

Table 2
Bimolecular rate constants for quenching of $Ru(dhcb)_3$ in solutions of 0.1 M ionic strength at 25 °C

Complex	pH	$k_q \times 10^{-9}$ (M^{-1} s^{-1})					
		$Fe(CN)_6^{3-}$	MV^{2+}	Cu^{2+}	$V^{2+}(PS^-)_2$	Nitrobenzene	O_2
In the absence of CTAB							
$Ru(dhcb)_3$	1	8.7	0.26	0.24	0.49	0.17	2.0
	3	1.5	2.4	2.8	0.87	0.85	2.1
	7	0.49	6.1 (5.6)[b]	2.8 (5.8)[b]	1.53	2.2	2.7
$Ru(bpy)_3^{2+}$	7	10	0.98	0.092	1.65	3.0	3.7
In the presence of 10 mM CTAB							
$Ru(dhcb)_3$	1	0[a]	0.27	0.23	0.44	0.15	1.8
	3	20	1.8	3.5	0.85	0.76	2.9
	7	16	2.8	0[a]	1.02	2.0	2.1

[a] Unable to measure due to the formation of precipitates.
[b] Reported values determined from lifetime data (Ref. 13).

where $\Delta h\nu$ is the difference between the emission maxima (in eV) of $Ru(bpy)_3^{2+}$ and the complex with ligand L: the superscripts L and bpy denote the ligands of the complexes.

Fig. 6 shows the cyclic voltammograms of $Ru(dhcb)_3$ taken in 2 M $HClO_4$ and at pH 5.6. The measured redox potentials of $Ru(dhcb)_3$ and the estimated values of $^*Ru(dhcb)_3$ (using Eq. (2)) are summarized in Table 3. The decreasing order of the magnitude of the oxidation potentials, i.e. the reducing power, is $^*Ru(bpy)_3^{2+} > {}^*Ru(dhcb)_3$ at pH $5.6 > {}^*Ru(dhcb)_3$ in 2 M $HClO_4$.

According to the theory of electron transfer quenching in highly polar medium, the free energy change ΔG_f of the reaction is given approximately by [22,23]

$$\Delta G_f = -E°(^*D/D^+) - E°(A/A^-) \quad (3)$$

where $E°(^*D/D^+)$ and $E°(A/A^-)$ are the oxidation potential of the excited state electron donor and the reduction potential of the electron acceptor respectively. The theory also predicts a diffusion-controlled rate constant when $\Delta G_f \leqslant -0.5$ eV and a sharp decrease in k_q values as ΔG_f increases from -0.5 eV. The reduction potentials of $V^{2+}(PS^-)_2$, nitrobenzene and O_2 are -0.40 V (measured in this work and approximately 80 mV more positive than previously reported data taken with an SnO_2-coated electrode [24]), -0.56 V [25] and -0.33 V [26] respectively. A strong dependence of k_q on $E°(^*D/D^+)$ is expected for these quenchers. The order of the magnitude of the oxidation potentials of the *Ru(II) complexes (Table 3) matches well the order of the quenching rate constants of the quenchers. Thus we can conclude that the pH dependence of the k_q values of reactions of $^*Ru(dhcb)_3$ with the zwitterionic and neutral quenchers in Table 2 arises from the pH dependence of the excited state oxidation potential of $Ru(dhcb)_3$. The difference between the k_q values for MV^{2+} ($E°(MV^{2+}/MV^+) = -0.45$ V) (measured in this work and approximately 80 mV more positive than previously reported data taken with an SnO_2-coated electrode [24]) for $Ru(bpy)_3^{2+}$ and $Ru(dhcb)_3$ at pH 1, where the complex is present as a dication, also reflects the difference between the

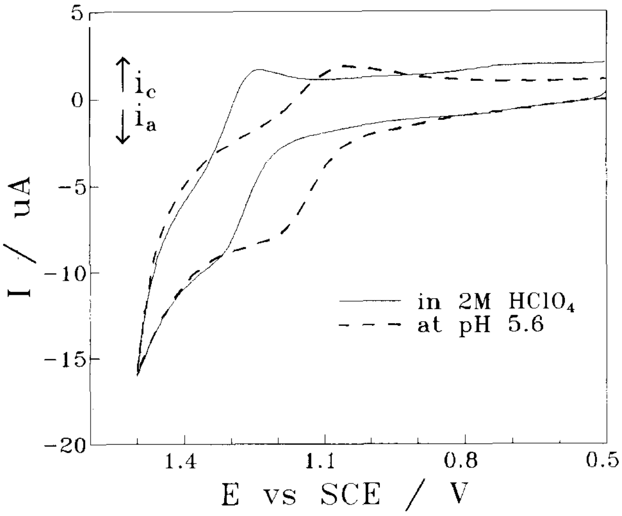

Fig. 6. Cyclic voltammograms of 1.0×10^{-3} M $Ru(dhcb)_3$ solutions: ——, in 2 M $HClO_4$; – – –, in 0.1 M $NaClO_4$ at pH 5.6. Electrode potentials are shown with respect to SCE.

Table 3
Redox potentials of $Ru(dhcb)_3$ and $Ru(bpy)_3^{2+}$ in aqueous media

Complex	Medium	$E(2+/3+)$[a] (V)	$h\nu$ (eV) (nm)	$E(^*2+/3+)$ (V)
$Ru(dhcb)_3$	2 M $HClO_4$	1.51 (1.56)[b]	1.90 (653)	0.52
	pH 5.6	1.36	1.93 (643)	0.70
$Ru(bpy)_3^{2+}$	0.1 M NaCl	1.26	1.97 (630)	0.84[c]

[a] Charges are only for Ru metal ion, not for metal complexes.
[b] Reported value obtained in 0.85 M H_2SO_4 (Ref. 8).
[c] Ref. 21 (see text).

oxidation potentials of the *Ru(II) complexes. In contrast, the k_q values for $Fe(CN)_6^{3-}$ are similar for both complexes because of the high reduction potential of the quencher (0.41 V) which gives a ΔG_f value much lower than -0.5 eV.

4. Conclusions

It has been shown that the six carboxylic acid groups of $Ru(dhcb)_3$ can be divided into two groups with respect to their acidity. Four have a ground state pK_a value of 3.7 and an excited state pK_a value of 8.2. The corresponding values for the remaining two carboxylic acid groups are 0.7 and 3.8 respectively. The complex is sparingly soluble in its inner salt form near pH 2. Protonation or deprotonation of the inner salt by a change from pH 2 increases the solubility of the complex. The complex behaves as a cationic form at $pH<2$ and an anionic form at $pH>3$. The emission intensity of the ionic form of the complex is greater and the emission maximum appears at shorter wavelengths than the zwitterionic (inner salt) form. The complex carrying net total charge binds to micelles with opposite charge. The oxidation potential of $*Ru(dhcb)_3$ is lower in acidic medium than in neutral medium, which, in turn, is lower than that of $Ru(bpy)_3^{2+}$. The rates of emission quenching depend on the electrostatic interaction between the reacting pairs, the chelation of the quencher to the carboxylate groups of the ligands of the complex and the oxidation potential of the complex. The k_q values of $Ru(dhcb)_3$ for neutral quenchers decrease as the pH of the medium is decreased due to the decrease in the oxidation potential of the *Ru(II) complex.

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