Photosensitized Generation of Singlet Oxygen from (Substituted Bipyridine)ruthenium(II) Complexes

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Dedicated to Prof. *André M. Braun* on the occasion of his 60th birthday

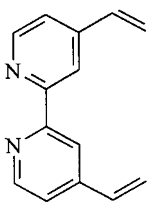
Photophysical properties in dilute MeCN solution are reported for seven Ru^{II} complexes containing two 2,2′-bipyridine (bpy) ligands and different third ligands, six of which contain a variety of 4,4′-carboxamide-disubstituted 2,2′-bipyridines, for one complex containing no 2,2′-bipyridine, but 2 of these different ligands, for three multinuclear Ru^{II} complexes containing 2 or 4 $[Ru(bpy)_2]$ moieties and also coordinated *via* 4,4′-carboxamide-disubstituted 2,2′-bipyridine ligands, and for the complex $[(Ru(bpy)_2(L)]^{2+}$ where L is *N*,*N*′-([2,2′-bipyridine]-4,4′-diyl)bis[3-methoxypropanamide]. Absorption maxima are red-shifted with respect to $[Ru(bpy)_3]^{2+}$, as are phosphorescence maxima which vary from 622 to 656 nm. The lifetimes of the lowest excited triplet metal-to-ligand charge transfer states ^{3}MLCT in de-aerated MeCN are equal to or longer than for $[Ru(bpy)_3]^{2+}$ and vary considerably, *i.e.*, from 0.86 to 1.71 μs. Rate constants k_q for quenching by O_2 of the ^{3}MLCT states were measured and found to be well below diffusion-controlled, ranging from 1.2 to $2.0 \cdot 10^9$ dm^3 mol^{-1} s^{-1}. The efficiencies f_Δ^T of singlet-oxygen formation during oxygen quenching of these ^{3}MLCT states are relatively high, namely 0.53–0.89. The product of k_q and f_Δ^T gives the net rate constant k_q^1 for quenching due to energy transfer to produce singlet oxygen, and $k_q - k_q^1$ equals k_q^3, the net rate constant for quenching due to energy dissipation of the excited ^{3}MLCT states without energy transfer. The quenching rate constants were both found to correlate with ΔG^{CT}, the free-energy change for charge transfer from the excited Ru complex to oxygen, and the relative and absolute values of these rate constants are discussed.

Introduction. – Although the charge-transfer nature of the lowest excited state of tris(bipyridine)ruthenium(II) ($[Ru(bpy)_3]^{2+}$) and related compounds [1][2] is well established, it is clear that quenching by oxygen of the lowest excited state of these complexes, at least in nonaqueous solvents, results in efficient energy transfer since they have been shown to be good photosensitizers of singlet oxygen [3–14]. The relatively long lifetime of the triplet, metal-to-ligand charge-transfer states ^{3}MLCT of many Ru^{II} complexes results in oxygen quenching in air-saturated solutions being quite efficient [3–14] since rate constants k_q for oxygen quenching of these ^{3}MLCT states are typically in the range 10^8–10^{10} dm^3 mol^{-1} s^{-1}. However, there have been relatively few publications on the mechanism of quenching of electronically excited states of coordination complexes by O_2 compared with the hundreds of such studies made with organic molecules [15–39]. We would like to dedicate this paper to *André M. Braun* on the occasion of his 60th birthday since he is joint author of an important paper [6] in this field, on oxygen quenching of ^{3}MLCT states of a series of homoleptic $[RuL_3]$ complexes (where L is 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 2,2′-bipyrazine (bpz), 4,7-diphenyl-1,10-phenanthroline (dip), diphenyl 1,10-phenanthroline-4,7-disulfonate (dpds), and 1,10-phenanthroline-5-octadecanamide (poda)) in

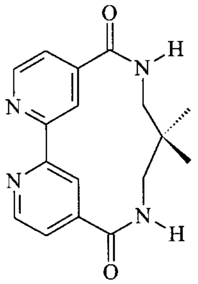
H_2O and MeOH, and on the resulting sensitized production of singlet oxygen. Thus, for example, *Braun* and co-workers [6] have reported quantum yields of singlet-oxygen production photosensitized by $[Ru(bpy)_3]^{2+}$ equalling 0.73 and 0.22 in CD_3OD and D_2O, respectively, relative to 1*H*-phenalen-1-one as a standard. These authors also measured k_q values and showed that the efficiency f_Δ^T of singlet-oxygen formation during oxygen quenching was unity for all the five Ru^{II} complexes which they investigated in MeOH. However, they observed that in D_2O, f_Δ^T values ranged from 0.44 to 1.0, with $f_\Delta^T = 0.48$ in the case of $[Ru(bpy)_3]^{2+}$, in agreement with the earlier value of *Mulazzani et al.* [8] who reported that the efficiency of photosensitized production of singlet oxygen by $[Ru(bpy)_3]^{2+}$ in D_2O equals 0.50, demonstrating that in aqueous solution, energy transfer only occurs in 50% of quenching events. Those complexes with the highest values for k_q tended to show the smallest f_Δ^T values, which *Braun* and co-workers [6] suggested was due to charge-transfer interactions similar to those first reported by us [16–23] for oxygen quenching of the triplet states of organic compounds, where an inverse correlation between k_q and the resulting efficiency f_Δ^T of singlet-oxygen formation is now firmly established for several classes of compounds.

In their early work, *Demas et al.* [12] reported oxygen quenching of the excited states of 16 luminescent diimine (bipyridine (bpy), phenanthroline (phen), and/or substituted phenanthroline) complexes of Ru^{II}, Os^{II}, and Ir^{III} in MeOH, with rate constants in the range 0.28 to $6.8 \cdot 10^9$ dm^3 mol^{-1} s^{-1}. These workers [12] found the quantum yield, Φ_Δ of singlet oxygen O_2^* ($^1\Delta_g$) production as a consequence of oxygen quenching of the excited ^{3}MLCT state of $[Ru(bpy)_3]^{2+}$ to be 0.86 in oxygen-saturated MeOH. Rate constants for oxygen quenching of the excited ^{3}MLCT states for caged and uncaged (polypyridine)ruthenium(II) complexes in MeCN have been reported [10] as $2.5 \cdot 10^9$ dm^3 mol^{-1} s^{-1} for the uncaged complex $[Ru(bpy)_3]^{2+}$, and $5.3 \cdot 10^8$ $dm^3 mol^{-1}$ s^{-1} for a fully caged complex. *Tanielian et al.* [14] have shown quenching of $[Ru(bpy)_3]^{2+}$ by O_2 to be solvent-dependent with k_q values varying from $1.4 \cdot 10^9$ dm^3 mol^{-1} s^{-1} in EtOH to $3.1 \cdot 10^9$ dm^3 mol^{-1} s^{-1} in MeCN and with Φ_Δ values in oxygen-saturated solutions in the range 0.41 to 0.87 yielding f_Δ^T values ranging from 0.58 to 0.92 on changing solvent from H_2O to MeOH.

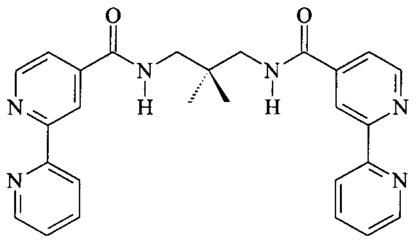
Recently [4], we have reported that in MeCN, the rate constants k_q for quenching by O_2 of the ^{3}MLCT states of (benzoaza-crown-substituted bipyridine)ruthenium(II) complexes were in the range 2.4 to $4.6 \cdot 10^9$ dm^3 mol^{-1} s^{-1}. Efficiencies f_Δ^T of singlet-oxygen production, sensitized by these ruthenium complexes, were found [4] to be in the range 0.26–0.69. In addition, we have reported [3] for a structurally similar series of methoxybenzene- or vinyl-linked (benzo-crown-ether-substituted 2,2′-bipyridine)ruthenium(II) complexes, that the quenching rate constants, again with MeCN as solvent, were in the range $2.2–4.2 \cdot 10^9$ dm^3 mol^{-1} s^{-1}, and efficiencies f_Δ^T of singlet-oxygen production [3] were in the range 0.21 – 0.74. Once again, those complexes with the highest values of k_q tended to be those with lowest f_Δ^T values. In the present study, we extend our investigations to (substituted 2,2′-bipyridine)ruthenium(II) systems and some multinuclear Ru^{II} complexes, *i.e.*, to $[\{Ru(bpy)_2\}_x L^n]^{2x+}$ ($x = 1$ or 2, L^n = substituted 2,2′-bipyridine) and $[Ru(L^4)_2L^1]$, to examine the effect of structural environment on the photosensitized generation of singlet oxygen and on the mechanism of quenching.



L^1



L^2



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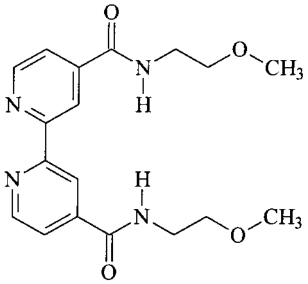
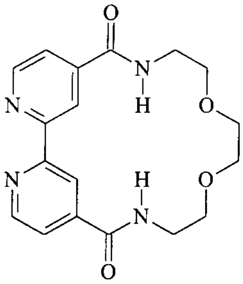
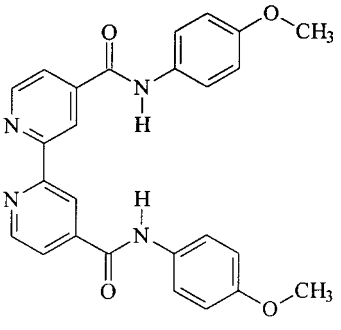


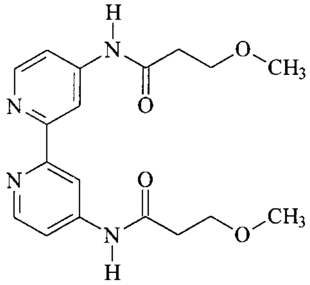
L^4



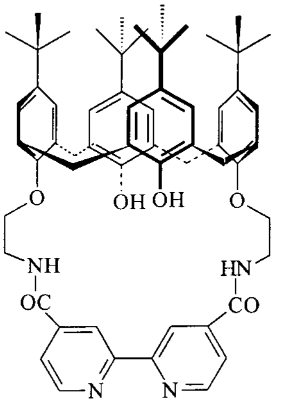
L^5



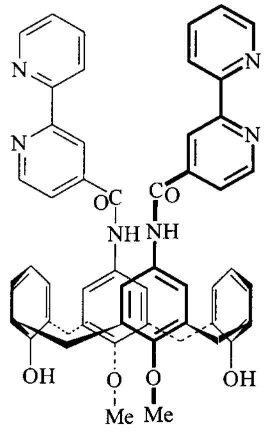
L^6



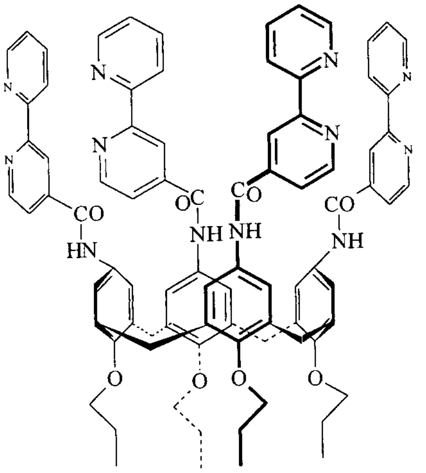
L^7



L^8



L^9



L^{10}

Experimental. – Acetonitrile (*Aldrich*, spectrophotometric grade) was dried by refluxing over CaH_2. Acridine (*Aldrich*) was recrystallized from MeOH. The compounds under investigation in this work which, in all cases but one (see later), have the general formula $[\{Ru(bpy)_2\}_xL^n]^{2x+}$ $[PF_6]_{2x}^-$ with $x = 1$ or 2, were available from previous studies [40]. With the exception of $[Ru(L^4)_2L^1]^{2+}$, they all contain at least one $[Ru(bpy)_2]$ moiety and one substituted bipyridine ligand L^n. The purity of the complexes has already been established (see [40]), and the lack of any luminescent impurities was confirmed by measuring the luminescence spectra at different excitation wavelengths and observing no spectral differences.

For singlet-oxygen luminescence measurements, the third harmonic of a *Lumonics Q*-switched Nd:YAG laser (*HY200*) was employed as a 355-nm excitation source. Time-resolved phosphorescence from air-saturated

MeCN solns. due to singlet-oxygen emission at 1270 nm was detected by an amplified *Judson* germanium photodiode (*J-16-85P-ROM5*, active diameter 0.5 cm). The laser energies employed were attenuated so as not to exceed 0.5 mJ per pulse. Individual luminescence traces (12 at least) were signal-averaged and were fitted by means of a single-exponential function to yield the luminescence intensity I_0 at $t = 0$. The luminescence intensity at zero time was measured at different laser intensities and compared with those obtained from optically matched solns. of acridine in MeCN as a standard ($\Phi_\Delta = 0.82$ [41]), thereby yielding relative Φ_Δ values. The observed rate constant for singlet-oxygen decay in MeCN was in agreement with literature values [42], *i.e.*, $1.25 \pm 0.1 \cdot 10^4$ s^{-1}. The same laser was used as the excitation source for kinetic measurements on the phosphorescence of the Ru complexes. The rate constants for oxygen quenching of the lowest excited state of Ru complexes (^{3}MLCT) were determined by following the phosphorescence decay in air-saturated solns. and in the corresponding degassed solutions (freeze-pump-thaw) monitoring for each compound at the emission maximum, as determined from steady state emission spectra. Eight single shot emission traces were signal-averaged for each measurement, and excellent single-exponential fits were obtained for all the phosphorescence decays in either the degassed or the air-saturated solutions. Transient absorption measurements performed with a nanosecond-laser-flash photolysis equipment give no evidence for the formation of oxidized species of the type $[(Ru(bpy)_2(L^n)]^{3+}$ or of ion pairs involving $[(Ru(bpy)_2(L^n)]^{3+}$ type ions being produced following oxygen quenching of the excited states of the studied complex ions in MeCN.

Results and Discussion. – The absorption spectra in dilute MeCN solution of a selection of the Ru^{II} complexes studied are shown in *Fig. 1*. It has been established that the metal-to-ligand charge-transfer (MLCT) absorption process produces mainly an excited singlet ^{1}MLCT state which undergoes intersystem crossing, populating the lowest ^{3}MLCT state with unit efficiency [1–4][43–45]. The absorption maximum of the metal-to-ligand charge-transfer bands for all the Ru^{II} complexes studied are red-shifted relative to $[Ru(bpy)_3]^{2+}$ the properties of which are given in *Table 1* for comparison. The luminescence spectra of some of the complexes are shown in *Fig. 1*, and band maxima are given in *Table 1*. The observed luminescence emission maxima of

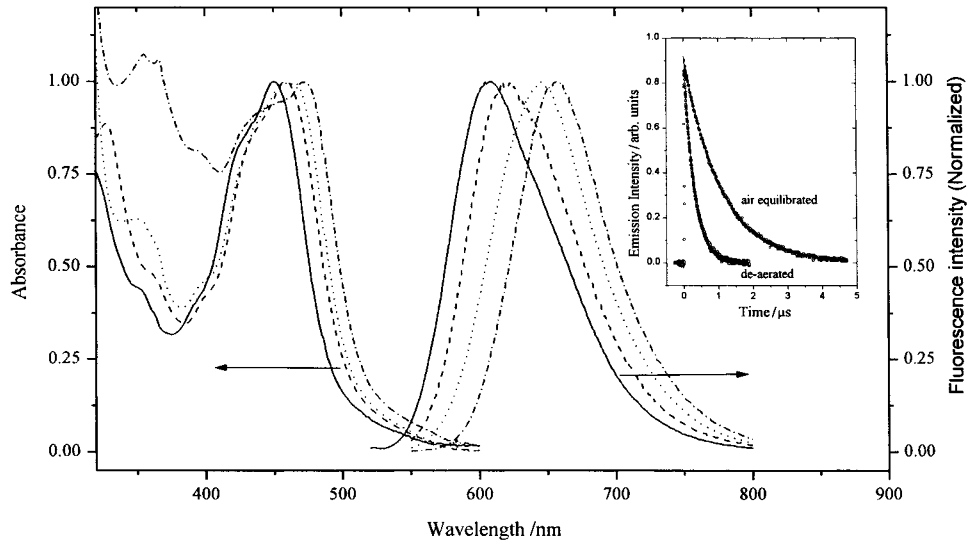


Fig. 1. *Absorption and luminescence spectra in MeCN of complexes* $[Ru(bpy)_3]^{2+}$ (——), $[Ru(bpy)_2(L^4)]^{2+}$ (⋯⋯), $[Ru(bpy)_2(L^6)]^{2+}$ (–·–·–), *and* $[Ru(bpy)_2(L^7)]^{2+}$ (- - - - -). Inset: phosphorescence decay at $\lambda_{em} = 646$ nm of the excited ^{3}MLCT state of $[Ru(bpy)_2(L^4)]^{2+}$ in MeCN in the presence and absence of oxygen.

Table 1. *Photophysical Properties of the (Substituted 2,2′-bipyridine)ruthenium(II) Complexes in MeCN*

	Φ_{Δ} a)	$P_{\mathrm{T}}^{\mathrm{O_2}}$ b)	f_{Δ}^{T} c)	$k_{\mathrm{q}}/10^{9}$ dm^{3} mol^{-1}s^{-1} d)	$\lambda_{\mathrm{abs}}^{\mathrm{max}}$/nm e)	$\lambda_{\mathrm{em}}^{\mathrm{max}}$/nm f)
[Ru(bpy)$_3$]$^{2+}$	0.57 ± 0.05	0.82	0.69	2.7 ± 0.2	451	607
[Ru(bpy)$_2$L^1]$^{2+}$	0.63 ± 0.06	0.87	0.73	2.0 ± 0.2	459	645
[Ru(bpy)$_2$L^2]$^{2+}$	0.48 ± 0.05	0.75	0.64	1.4 ± 0.1	473	654
[Ru(bpy)$_2$L^4]$^{2+}$	0.61 ± 0.06	0.72	0.85	1.2 ± 0.1	464	646
[Ru(bpy)$_2$L^5]$^{2+}$	0.52 ± 0.05	0.68	0.77	1.3 ± 0.1	471	656
[Ru(bpy)$_2$L^6]$^{2+}$	0.41 ± 0.04	0.75	0.55	1.3 ± 0.1	474	656
[Ru(bpy)$_2$L^7]$^{2+}$	0.61 ± 0.06	0.69	0.89	1.3 ± 0.1	459	622
[Ru(bpy)$_2$L^8]$^{2+}$	0.51 ± 0.05	0.71	0.72	1.2 ± 0.1	474	655
[Ru(L^4)$_2$L^1]$^{2+}$	0.51 ± 0.05	0.75	0.68	1.2 ± 0.1	471	646
[{Ru(bpy)$_2$}$_2$L^3]$^{4+}$	0.49 ± 0.05	0.81	0.61	1.7 ± 0.1	457	643
[{Ru(bpy)$_2$}$_2$L^9]$^{4+}$	0.41 ± 0.04	0.78	0.53	1.4 ± 0.1	458	645
[{Ru(bpy)$_2$ }$_4$L^{10}]$^{8+}$	0.43 ± 0.04	0.78	0.55	1.5 ± 0.1	459	644

a) Φ = Singlet oxygen quantum yield in air-equilibrated MeCN. b) $P_{\mathrm{T}}^{\mathrm{O_2}}$ = Fraction of the ^{3}MLCT states quenched by oxygen. c) f_{Δ}^{T} = Efficiency of singlet-oxygen production from the ^{3}MLCT states. d) k_{q} = rate constants for quenching of ^{3}MLCT states of Ru$^{\mathrm{II}}$ complexes by oxygen. e) $\lambda_{\mathrm{abs}}^{\mathrm{max}}$ = Wavelength of maximum absorption. f) $\lambda_{\mathrm{em}}^{\mathrm{max}}$ = Wavelength of maximum emission.

the ^{3}MLCT bands show more clearly the effect of ligand variation on excited-state energies; for example, the emission maxima occur at 607, 622, 645, and 656 nm for [Ru(bpy)$_3$]$^{2+}$, [Ru(bpy)$_2$ (L^7)]$^{2+}$, [Ru(bpy)$_2$(L^1)]$^{2+}$, and [Ru(bpy)$_2$ (L^6)]$^{2+}$ respectively. The size of the spectral shift can be seen to depend on the extent of conjugation within the ligands with similar substituents.

The literature value [1] for the energy of the lowest vibrational level of the ^{3}MLCT state above the ground state, E_{00}, for [Ru(bpy)$_3$]$^{2+}$ in MeCN is reported to be 205 kJ mol^{-1}, *i.e.*, 8 kJ mol^{-1} greater than the energy corresponding to the luminescence emission maximum. We assumed that E_{00} values for all these tris(bipyridine)-type complexes can be calculated by adding 8 kJ mol^{-1} to the energy corresponding to the longest wavelength luminescence emission maximum of the ^{3}MLCT band, and E_{00} values calculated in this way are listed in *Table 2*. It can be seen that the energy E_{00} for all complexes is 193 ± 3 kJ mol^{-1}, except for [Ru(bpy)$_2$(L^7)]$^{2+}$ where E_{00} is 200 kJ mol^{-1}. Note that the ligand L^7 is the only ligand used here where the 2,2′-bipyridine 4,4′-disubstitution is *via* the amino group of the carboxamide moiety.

Electrochemical measurements demonstrate that each complex undergoes one or two oxidation and several reduction processes. It is well known that [Ru(bpy)$_3$]$^{2+}$ undergoes an oxidation process centred at the Ru^{2+} ion and a series of reduction waves corresponding to successive one-electron reduction of the three bidentate ligands. For the majority of the complexes, the observed shapes of the cyclic voltammograms of the higher oxidation waves, assigned as $E_{3+/2+}^{\mathrm{ox}}$ in *Table 2*, are close to those expected for reversible systems. In the case of [Ru(bpy)$_2$(L^6)]$^{2+}$, the conjugated ligand irreversible oxidation process overlaps the metal-based redox wave and, therefore, the half-peak potential $E_{\mathrm{p}}/2$ is given, rather than $E_{3+/2+}^{\mathrm{ox}}$. As can be seen from *Table 2*, all the complexes, except for [Ru(bpy)$_2$(L^7)]$^{2+}$, show $E_{3+/2+}^{\mathrm{ox}}$ values within the range 1.4 ± 0.1 V *vs.* SCE, *i.e.*, slightly larger than the parent [Ru(bpy)$_3$]$^{2+}$ (1.28 V *vs.* SCE [3]).

The luminescence decay of the excited state of the investigated complexes in the presence and absence of oxygen can be fitted well by mono-exponential decays, see

Table 2. *Lifetime τ^0 of the Excited ^{3}MLCT States, Energy* E_{00} *of the 0-0 Transition Oxidation Potentials* $E^{ox}_{3+/2+}$ *of the Ru Complexes in MeCN, Net Rate Constant* k^1_q *for Quenching Due to Energy Transfer to Produce Singlet Oxygen, and Net Rate Constant* k^3_q *for Quenching Due to Energy Dissipation of the Excited ^{3}MLCT States without Energy Transfer, and Free Energy Change* ΔG^{CT}*, in MeCN Calculated by* Eqn. 6 *taking* $C = 0$

	τ^0/µs a)	E_{00}/ kJ mol^{-1}	$E^{ox}_{3+/2+}$/ V *vs.* SCE b)	k^1_q/ 10^9 dm^3 mol^{-1}s^{-1} c)	k^3_q/ 10^9 dm^3 mol^{-1}s^{-1} d)	ΔG^{CT}/ kJ mol^{-1}
$[Ru(bpy)_3]^{2+}$	0.87	205	1.28	1.9	0.9	– 6.2
$[Ru(bpy)_2L^1]^{2+}$	1.71	193	1.26	1.5	0.5	3.8
$[Ru(bpy)_2L^2]^{2+}$	1.14	191	1.35	0.9	0.5	14.5
$[Ru(bpy)_2L^4]^{2+}$	1.06	193	1.45	1.1	0.2	22.2
$[Ru(bpy)_2L^5]^{2+}$	0.88	190	1.34	1.0	0.3	14.5
$[Ru(bpy)_2L^6]^{2+}$	1.19	190	1.38 e)	0.7	0.6	18.4
$[Ru(bpy)_2L^7]^{2+}$	0.86	200	1.18	1.2	0.2	– 10.9
$[Ru(bpy)_2L^8]^{2+}$	1.13	191	1.45	0.8	0.3	24.2
$[Ru(L^4)_2L^1]^{2+}$	1.32	193	1.36	0.8	0.4	13.5
$[\{Ru(bpy)_2\}_2L^3]^{4+}$	1.28	194	1.31	1.1	0.7	7.7
$[\{Ru(bpy)_2\}_2L^9]^{4+}$	1.32	193	1.49	0.7	0.7	26.0
$[\{Ru(bpy)_2\}_4L^{10}]^{8+}$	1.26	194	1.34	0.8	0.7	10.5

a) Error ±5%. b) ±0.02 V *vs.* SCE. c) Error ±20%. d) Values calculated by *Eqn. 5* are subject to error values of 20% or higher when f^T_Δ approaches unity. e) Irreversible behaviour; the value given is the half wave peak potential ($E_p/2$); see text.

inset of *Fig. 1*. The ^{3}MLCT phosphorescence lifetime is found to be quite sensitive to ligand variation, with lifetimes of the excited ^{3}MLCT states varying from 0.86 to 1.71 µs. These lifetimes are close to or longer than the lifetime of the parent $[Ru(bpy)_3]^{2+}$ (see *Table 2*). The increase in lifetime is consistent with the ligands inhibiting the solvent-induced electronic to vibrational radiationless transition probably due to the decreased mixing of the excited metal-to-ligand charge-transfer state (^{3}MLCT) with the excited metal-centered (MC) state as the energy of ^{3}MLCT for all complexes are lower than that of the prototype complex $[Ru(bpy)_3]^{2+}$ [3]. To elucidate the relative contribution of the nonradiative processes to the lifetime of these Ru^{II} complexes, temperature-dependent emission lifetime measurements were undertaken. The pseudo-first order decay constant in air-saturated solutions, k_{obs}, is given by *Eqn. 1*, where k^0 is the intrinsic first order decay constant of the ^{3}MLCT state in the absence of oxygen ($=1/\tau^0$). Values of k_q, the rate constants for quenching by oxygen, were obtained by *Eqn. 1* taking the oxygen concentration in air-saturated MeCN solution as $1.9 \cdot 10^{-3}$ mol dm^{-3} [46].

$$k_{obs} = k^0 + k_q\,[O_2] \tag{1}$$

The values of k_q obtained in this work are listed in *Table 2*. They lie in the range $1.1 - 2.0 \cdot 10^9$ dm^3 mol^{-1} s^{-1} and are in every case lower than the oxygen-quenching rate constants k_q for $[Ru(bpy)_3]^{2+}$ which is $2.75 \cdot 10^9$ dm^3 mol^{-1} s^{-1} [3]. It is interesting to compare these values of k_q with k_d, the diffusion-controlled rate constant. Using the *Smoluchowski* equation [47] for reaction of $[Ru(bpy)_3]^{2+}$ with oxygen in MeCN at 298 K, based on effective radii of 7.1 and 2 Å for $[Ru(bpy)_3]^{2+}$ and oxygen, respectively, and taking the viscosity as 0.345 cP for MeCN [46], k_d was calculated to be $2.8 \cdot 10^{10}$ dm^3 mol^{-1} s^{-1}. This value is close to $2.1 \cdot 10^{10}$ dm^3 mol^{-1} s^{-1} found experimentally [48] as the limiting value for redox quenching of the ^{3}MLCT state of $[Ru(bpy)_3]^{2+}$ in MeCN in studies where the quenchers were somewhat larger than O_2. The complexes under investigation in this study show a wide variation in size, particularly the multinuclear complexes; however, all the complexes but one contain at least one $[Ru(bpy)_2]$ moiety, and it is well known that changing molecular size of one partner in a bimolecular reaction has little effect on the diffusion-controlled rate constant [47]. Based on the calculated value of k_d for $[Ru(bpy)_3]^{2+}$, it is apparent that in all these cases, k_q, the oxygen-quenching rate constants for tris(bipyridyl)ruthenium(II) complexes in MeCN are less than $k_d/9$ ($3.1 \cdot 10^9$ dm^3 mol^{-1} s^{-1}) where 1/9 is the spin statistical factor expected if quenching only occurred from singlet encounter complexes of the two triplet states undergoing reaction. In the case of oxygen quenching of the triplet states of organic compounds, values of oxygen-quenching constants k_q greater than $k_d/9$ have been observed, but rarely when energy transfer to produce singlet oxygen is 100% efficient.

The quantum yield of singlet-oxygen production Φ_Δ arising from oxygen quenching of the triplet metal-to-ligand charge transfer state (^{3}MLCT) of the Ru complexes is given by *Eqn. 2*, where Φ_T is the efficiency of population of the lowest excited ^{3}MLCT state, f_Δ^T is the fraction of triplet states quenched by oxygen which yield $O_2{}^*$ ($^1\Delta_g$), and $P_T^{O_2}$ is the fraction of the ^{3}MLCT states quenched by oxygen, as defined by *Eqn. 3*.

$$\Phi_\Delta = \Phi_T \, P_T^{O_2} \, f_\Delta^T \tag{2}$$

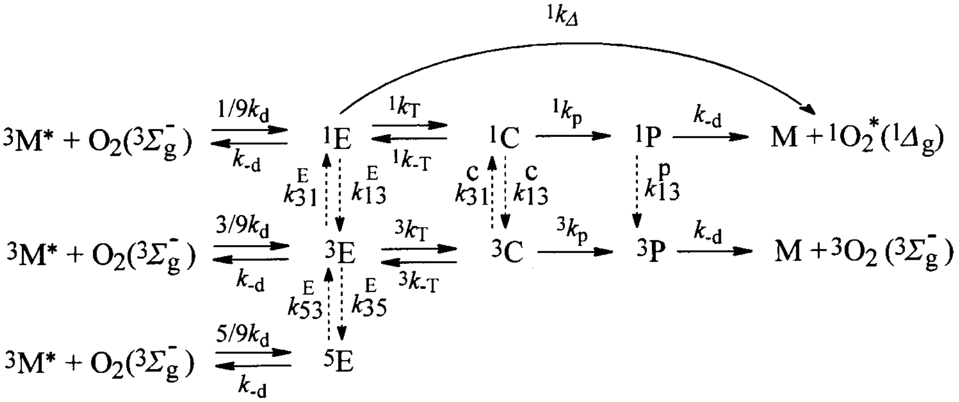
$$P_T^{O_2} = \frac{k_q\,[O_2]}{k^0 + k_q\,[O_2]} \tag{3}$$

All indications are that the quantum yield of intersystem crossing to the lowest excited ^{3}MLCT state is unity for $[Ru(bpy)_3]^{2+}$ and other Ru^{II} complexes [1][2]. In agreement with this, *Braun* and co-workers [6] showed that $\Phi_T = 1$ for $[Ru(bpz)_3]^{2+}$ in D_2O and CD_3OD, where bpz = 2,2′-bipyrazine, since they obtained identical values (within exper. error) for Φ_Δ and $P_T^{O_2}$. The rise time, measured for the production of the lowest excited state of $[Ru(bpy)_3]^{2+}$ following excitation into the spin-allowed excited state, of ≤ 1 ns confirms, as expected due to the heavy-atom effect, that in the presence of Ru, intersystem crossing to the ^{3}MLCT state is very fast. Since Φ_T, the efficiency of population of the lowest excited spin-forbidden ^{3}MLCT state, can be taken as unity, it follows that $\Phi_\Delta = P_T^{O_2} f_\Delta^T$. Φ_Δ Values in MeCN were measured relative to the reference acridine for which a value of 0.82 has been reported [35]. Values of Φ_Δ, $P_T^{O_2}$, and f_Δ^T are listed in *Table 1*.

The mechanism of quenching by oxygen of the triplet states of organic compounds given in the *Scheme* was first introduced by *Gijzeman et al.* [28], who stressed the importance of spin statistical factors. This mechanism was later extended by us [18–20][25] to include charge-transfer intermediates to account for quenching rate constants, which depend on the oxidation potential of the triplet state being quenched, and in several cases gave values higher than one ninth of the diffusion-controlled rate constant k_d.

In the *Scheme*, $^3M^*$ represents the excited triplet state of the sensitizer, $^{1,3,5}E$ represent the encounter complexes $^{1,3,5}(^3M^* .. {}^3O_2\,(^3\Sigma_g{}^-))$, $^{1,3}C$ represent the charge-

Scheme



transfer complexes ${}^{1,3}({}^{2}M^{\delta+}..{}^{2}O_2{}^{\delta-})$, ${}^{1}P$ represents the precursor complex ${}^{1}({}^{1}M..{}^{1}O_2{}^{*}({}^{1}\Delta_g))$, and ${}^{3}P$ the precursor complex ${}^{3}({}^{1}M..{}^{3}O_2({}^{3}\Sigma_g{}^{-}))$. The question whether any or all of the intersystem crossings shown in the *Scheme* as dotted arrows occur between the singlet, triplet, and quartet spin channels, when MeCN at room temperature is used as solvent, is still open to debate (see, *e.g.*, [16–20][25][33]). It might be expected that during oxygen quenching of the ^{3}MLCT excited state of (substituted bipyridine)ruthenium(II) systems, the presence of the heavy ion Ru^{II}, would enhance spin-forbidden pathways, possibly inducing intersystem crossing between singlet, triplet, and quintet channels as shown in the *Scheme.* However, the fact that k_q in all cases is less than even $k_d/9$ does not support their occurrence here.

According to the *Scheme*, the total quenching rate constant k_q is equal to the sum of the rate constants k_q^1 for quenching *via* the singlet channel resulting in singlet-oxygen formation and the rate constant k_q^3 for quenching *via* the triplet channel which leads to deactivation of the excited states without generating singlet oxygen, *i.e.*, $k_q = k_q^1 + k_q^3$ where

$$k_q^1 = k_q\, f_\Delta^T \tag{4}$$

$$k_q^3 = k_q\,(1 - f_\Delta^T) \tag{5}$$

The free energy for electron-transfer quenching of excited Ru^{II} complexes is expected to depend on the redox parameters and the excitation energies of the interacting species as given by *Rehm* and *Weller* [50] according to *Eqn. 6*, where F is the Faraday constant, and $E_{O_2}^{red}$ is the half-wave reduction potential for oxygen taken as -0.78 V *vs.* SCE [51]. The Coulomb term C is often neglected, especially in polar solvents such as MeCN since $\varepsilon = 37$. Values of ΔG^{CT} taking $C = 0$ are given in *Table 2*, and *Fig. 2* shows the dependence of k_q and k_q^1 on ΔG^{CT} for the Ru^{II} complexes (k_q^3 also shows a similar dependence on ΔG^{CT}, but with considerable scatter because of the combined errors in k_q and particularly in $(1 - f_\Delta^T)$ as f_Δ^T approaches unity). As mentioned earlier, transient-

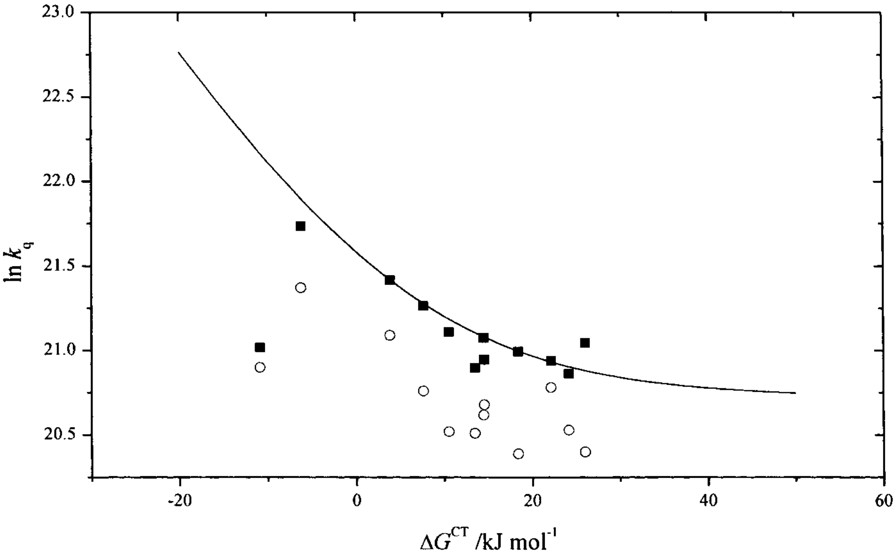


Fig. 2. *Dependence of the logarithm of oxygen-quenching rate constants of the* ^{3}*MLCT excited state of Ru*^{II} *complex ions on the free-energy change* ΔG^{CT} *for charge transfer from excited Ru complexes to* O_2 ($^3\Sigma_g^-$) *in MeCN* k_q (■), *and* k_q^1 (○). The solid curve is obtained with the equation $k_q = k_q^{ev} + A\exp(-\Delta G^{\neq}/RT)$; see text.

absorption measurements with a nanosecond-laser-flash photolysis equipment give no evidence of ions or ion pairs containing Ru^{III}.

$$\Delta G^{CT} = F\,[E^{ox}_{(3+/2+)} - E^{red}_{O_2}] - E_{00} + C \qquad (6)$$

According to the *Scheme*, developed for organic sensitizers [16–20][25][28], one expects $k_q^1 = k_q^{ev} + k_q^{cta}$, *i.e.*, two contributions, the first, k_q^{ev}, arising from direct energy transfer from encounter complexes without charge-transfer character, and a second contribution k_q^{cta}, which involves the charge transfer assisted production of singlet oxygen. The solid curve drawn in *Fig. 2*, which fits the data quite well, has the form $k_q = k_q^{ev} + k_q^{cta}$, with $k_q^{cta} = A\exp(-\Delta G^{\neq}/RT)$, with $k_q^{ev} = 1.0 \cdot 10^9$ dm^3 mol^{-1} s^{-1}, $A = 2.7 \cdot 10^{12}$ dm^3 mol^{-1} s^{-1}, and $\Delta G^{\neq} = 19$ kJ mol^{-1} + $0.2\,\Delta G^{CT}$.

The absolute value of $k_q^{ev} = 10^9$ dm^3 mol^{-1} s^{-1} needed for to fit the experiment data is comparable with the values determined for energy transfer in CCl_4 [38] for organic triplet states with triplet energy equal to 192 ± 2 kJ mol^{-1}. The linear free energy relationship used for $\Delta G^{\neq}$ is similar to that used previously [18–20] and can be taken to imply that the exciplex through which charge transfer assisted quenching occurs has partial charge transfer with $\delta \approx 20\%$. k_q^3 may be considered as also having 2 components; however, the total catalysed conversion of all 192 kJ mol^{-1} of electronic energy to vibrational energy in the absence of charge-transfer assistance is likely to make only a small contribution to quenching without energy transfer.

It is obvious that the data from [(Ru(bpy)$_2$(L^7)]$^{2+}$ where L^7 is *N,N'*-([2,2'-bipyridine]-4,4'-diyl)bis[3-methoxypropanamide], which is the only Ru^{II} complex which does not contain [2,2′-bipyridine]-4,4′-dicarboxamide ligands, does not fall even near the curve drawn in *Fig. 2* for the other complexes. This is the only amide-substituted 2,2′-bipyridine ligand whose amide function is attached by the amino moiety, and probably, the photoexcited electron that participates in the charge transfer to molecular oxygen resides on the bpy moiety and not on the side chains of L^7, whereas for the rest of the complexes, the 'electron' contributing to charge-transfer quenching is likely to reside on the attached amide moieties.

It is interesting to note that the total quenching rate constants k_q for these complexes are in every case less than for $[Ru(bpy)_3]^{2+}$, whereas for several (benzoaza[15]crown-5-bipyridine)ruthenium(II) complexes studied by us previously [4], k_q values were in all cases higher than for $[Ru(bpy)_3]^{2+}$. This demonstrates that the nature of the ligand affects the results, and this needs to be considered as well properties such as E_{00} and ΔG^{CT}.

The multinuclear complexes give rate constants for quenching which show no clear dependence on the number of Ru^{II} centres in the quencher. Only for one of the three multinuclear complexes, *i.e.*, in the case of $[\{Ru(bpy)_2\}_2L^9]^{4+}$, there is any indication that the presence of more than one Ru^{II} in the molecule leads to a somewhat higher value of k_q. There is little indication of large steric effects affecting the k_q values in any of these compounds.

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