106. Singlet-Oxygen ($^1\Delta_g$) Production by Ruthenium(II) Complexes Containing Polyazaheterocyclic Ligands in Methanol and in Water

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In the context of our studies on ruthenium(II) complexes containing polyazaheterocyclic ligands, we have determined the rate constants of quenching by molecular oxygen (k_q) of the metal-to-ligand charge-transfer-excited state of a series of homoleptic [RuL_3] complexes (where L stands for 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 in MeOH. These compounds are singlet-oxygen ($O_2(^1\Delta_g)$) sensitizers, and quantum yields of singlet-oxygen production (Φ_Δ) in both solvents are also reported. Values of k_q and Φ_Δ depend on the nature of the ligand L and on the solvent, Φ_Δ values showing a large range of variation (0.2 to 1.0). In MeOH, the only pathway for quenching of the excited [RuL_3] complexes by molecular oxygen is energy transfer: the fraction of quenched excited states yielding singlet oxygen (f_Δ^T) is unity for all compounds in the series investigated. Changing from MeOH to H_2O has several remarkable effects: higher k_q and lower Φ_Δ values are observed; f_Δ^T drops to *ca.* 0.5 except for $[Ru(bpz)_3]^{2+}$. In fact, $[Ru(bpz)_3]^{2+}$ is by far the weakest reductant in the series and behaves differently from the other complexes, with lowest k_q and Φ_Δ values and a f_Δ^T equal to 1 in both solvents. Results are interpreted on the basis of the role played by charge-transfer interactions between the sensitizer excited state and molecular oxygen in the quenching mechanism. Ru^{II} Complexes based on the 4,7-diphenyl-1,10-phenanthroline (dip) ligand are very efficient and stable singlet-oxygen sensitizers with Φ_Δ values close to unity in air-saturated MeOH.

1. Introduction. – Singlet oxygen ($O_2(^1\Delta_g)$), the lowest electronically excited state of the oxygen molecule, is a highly reactive species and a key intermediate in chemical and biological processes, such as photooxidation reactions, DNA damage, and photodynamic therapy of cancer [1–5]. Most often, singlet oxygen is produced by photosensitization involving electronic-energy transfer from the triplet excited state of a sensitizer (generally a dye) to ground-state molecular oxygen. Investigations on sensitizers able to produce efficiently singlet oxygen, as well as studies aimed at elucidating the role of the solvent or the surrounding medium, are of great interest because of the importance of singlet oxygen in both photochemical and photobiological applications.

Coordination compounds of Ru^{II} with polyazaheteroaromatic chelating ligands have attracted considerable attention during the last fifteen years. This is due to the unique combination of their spectroscopic, redox, and photochemical features, together with the possibility of 'fine tuning' their properties by a judicious choice of the type, number, and substituents of the heteroaromatic chelating ligands of the metal coordination sphere [6]. The excitation of Ru^{II} chelate complexes in the 180–550-nm spectral region is followed by a fast intersystem crossing leading to the formation of the metal-to-ligand charge-transfer triplet excited state (^{3}MLCT). Due to its highly oxidizing and reducing potentials, this rather short lived luminescent ^{3}MLCT state (0.1 to 5 μs in deoxygenated solutions at room temperature) is able to participate in both energy and electron-transfer reactions with a variety of organic and inorganic species [7]. Quenching of the ^{3}MLCT state by molecular oxygen was reported as early as 1972 [8]. In subsequent studies, the mechanism of the bimolecular deactivation process has been investigated (see *e.g.*, [9–14]), but no general agreement may be found in the published conclusions. Both, efficient singlet-oxygen formation by energy transfer from the ^{3}MLCT excited state to the oxygen molecule [9] [13] [15] and predominant electron-transfer quenching to give superoxide anion [14] [16] [17] have been reported.

To get further insight into the mechanism of quenching of the ^{3}MLCT state of this type of compounds and to evaluate the importance of solvent effects on the quenching process, we have undertaken an investigation using homoleptic Ru^{II}-diimine complexes (denoted below as $[RuL_3]$) in which the nature of the coordinating ligand has been varied. A series of $[RuL_3]$ complexes, where L stands for 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) have been investigated. In this paper, we report the rate constants of quenching of the ^{3}MLCT state by molecular oxygen (k_q) and the quantum yields of singlet-oxygen production (Φ_Δ) in H_2O and MeOH solutions. The differences observed in the two solvents are discussed in terms of the role played by charge-transfer interactions in the quenching mechanism.

2. Spectroscopic Properties of the [RuL$_3$] Complexes Investigated and Quenching of Their Excited State by Molecular Oxygen.

– The absorption and emission spectra of the $[RuL_3]$ complexes investigated, as well as their emission lifetimes (τ), were measured in Ar-, air- and O_2-saturated MeOH and H_2O solutions (except for $[Ru(poda)_3]^{2+}$ which is not soluble in H_2O). Deuterated solvents have been used for comparison with singlet-oxygen luminescence measurements (see *Exper. Part*). The corresponding absorption and emission characteristics are collected in *Tables 1* and *2*.

The bimolecular rate constants of the quenching of the $[RuL_3]$ emission by molecular oxygen (k_q) have been determined from the slopes of the linear *Stern-Volmer* plots ($\tau_0/\tau = 1 + k_q\tau_0\,[O_2]$) calculated with the values of the emission lifetimes in the absence and in the presence of oxygen (τ_0 and τ, respectively). The data have been obtained by single-photon-counting (SPC) measurements (*Table 2*). Identical values of k_q (within experimental error) have been calculated from the slopes of *Stern-Volmer* plots obtained from steady-state emission-quenching experiments ($I_0/I = 1 + k_q\tau_0\,[O_2]$). In fact, both procedures should yield identical results, provided that quenching by molecular oxygen be purely diffusional [18]. At concentrations used in the time-resolved experiments (in general, 1.2×10^{-5} mol l^{-1} to 1.4×10^{-4} mol l^{-1}), a sum of two or three exponentials were required to achieve a satisfactory fit of the emission decay profiles of $[Ru(dip)_3]^{2+}$ in D_2O and of $[Ru(poda)_3]^{2+}$ in CD_3OD. In these cases, mean lifetimes ($<\tau> = \Sigma A_i\tau_i^2/\Sigma A_i\tau_i$ [18]) are reported in *Table 2*, and k_q values have been calculated from steady-state emission-quenching experiments. The multi-exponential decay kinetics observed are probably due to the scarce solubility of the hydrophobic $[Ru(dip)_3]^{2+}$ in H_2O and to the presence of long aliphatic chains in $[Ru(poda)_3]^{2+}$ which lead to significant self-aggrega-

Table 1. *Absorption Characteristics of the [RuL$_3$] Complexes Investigated in Water and in Methanol*[a])

[RuL$_3$]	λ (CH$_3$OH) [nm]	ε (CH$_3$OH) [l mol^{-1} cm^{-1}]	λ (H$_2$O) [nm]	ε (H$_2$O) [l mol^{-1} cm^{-1}]
[Ru(bpy)$_3$]$^{2+}$	449 (λ_{max})	13850	452 (λ_{max})	14000 [6]
	437	13600	437	12600[b])
	367	4300		
[Ru(phen)$_3$]$^{2+}$	444 (λ_{max})	17350	447 (λ_{max})	19000 [6]
	437	16850	437	18450[b])
	367	7050		
[Ru(bpz)$_3$]$^{2+}$	440 (λ_{max})	12900	443 (λ_{max})	15000 [6]
	437	12800	437	15000[b])
	367	3400		
[Ru(dip)$_3$]$^{2+}$	462 (λ_{max})	29450	460 (λ_{max})	29500
	437	29100	437	29500
	367	6950		
[Ru(dpds)$_3$]$^{4-}$	463 (λ_{max})	32400	462 (λ_{max})	29300
	437	32100	437	29100
	367	7900		
[Ru(poda)$_3$]$^{2+}$	449 (λ_{max})	17750	[c])	[c])
	437	16650		
	367	6650		

[a]) At room temperature; standard deviation: $\lambda \pm 1$ nm, $\varepsilon \pm 2$–3%.

[b]) Calculated from the absorption maxima given in [6] and from the spectra recorded during this work.

[c]) [Ru(poda)$_3$]$^{2+}$ is not soluble in water.

Table 2. *Emission Wavelengths, Emission Lifetimes, and Bimolecular Rate Constants of Emission Quenching by Molecular Oxygen for the [RuL$_3$] Complexes Investigated in D$_2$O and in CD$_3$OD*

[RuL$_3$]	Solvent	λ_{em} [nm][a])	τ_0 [ns] Ar	τ [ns] air	τ [ns] O$_2$	k_q[c]) [l mol^{-1} s^{-1}]
[Ru(bpy)$_3$]$^{2+}$	CD$_3$OD	623 (621)	788	228	61	1.9×10^9
	D$_2$O	622 (629)	1005	558	203	3.3×10^9
[Ru(phen)$_3$]$^{2+}$	CD$_3$OD	592 (594)	296	124	37	3.0×10^9
	D$_2$O	600	1154	545	180	4.0×10^9
[Ru(bpz)$_3$]$^{2+}$	CD$_3$OD	(626)	946	614	307	2.7×10^8
	D$_2$O	621	1302	1136	701	5.6×10^8
[Ru(dip)$_3$]$^{2+}$	CD$_3$OD	(619)	5944	241	52	2.4×10^9
	D$_2$O	638 (632)	5287[b])	949[b])	211[b])	3.3×10^9[d])
[Ru(dpds)$_3$]$^{4-}$	CD$_3$OD	624 (618)	5572	314	67	1.8×10^9
	D$_2$O	632 (632)	5742	1070	270	2.9×10^9
[Ru(poda)$_3$]$^{2+}$	CD$_3$OD	603 (598)	665[b])	192[b])	54[b])	1.7×10^9[d])

[a]) Corrected values; values in parentheses are those in the corresponding non-deuterated solvents.

[b]) Bi- or tri-exponential decays except for [Ru(poda)$_3$]$^{2+}$ in air-saturated methanol; reported data are the mean lifetimes ($<\tau> = \Sigma A_i\tau_i^2/\Sigma A_i\tau_i$ [18]).

[c]) Standard deviation: ● 8%; in CD$_3$OD, $k_{en} = k_q$.

[d]) Calculated from steady-state emission quenching experiments (see text).

tion. In fact, a single exponential decay profile has been observed for both compounds at sub-micromolar concentrations. Note also that fortuitously the emission decay of $[Ru(poda)_3]^{2+}$ in air-saturated CD_3OD can be fitted to a single exponential. Some τ_0 and k_q values, in MeOH or in H_2O, for the $[RuL_3]$ complexes investigated in this work (except for $[Ru(poda)_3]^{2+}$) have already been reported in the literature [6] [7] [12] [13] [15] [19]. Our results are in good agreement with these previous determinations.

3. Quantum Yields of Singlet-Oxygen Production. – 3.1. *Theoretical.* To establish the theoretical expression relating the quantum yield of singlet-oxygen production (Φ_Δ) to the sensitizer excited-state parameters, the various photophysical and photochemical pathways involved have to be considered. Using $[RuL_3]$ complexes as sensitizers, singlet oxygen ($O_2(^1\Delta_g)$, denoted as $^1O_2$) is produced by energy transfer from the ^{3}MLCT excited state ($^3[RuL_3]^*$) to molecular oxygen ($O_2(^3\Sigma_g^-)$, denoted as O_2) (*Eqns. 1* and *2*).

$$[RuL_3] \xrightarrow{h\nu} {}^1[RuL_3]^* \xrightarrow{k_{ISC}} {}^3[RuL_3]^* \tag{1}$$

$$^3[RuL_3]^* + O_2 \xrightarrow{k_{en}} [RuL_3] + {}^1O_2 \tag{2}$$

Competing monomolecular processes from $^3[RuL_3]^*$ are radiative and nonradiative deactivation (*Eqns. 3* and *4*).

$$^3[RuL_3]^* \xrightarrow{k_r} [RuL_3] + h\nu'' \tag{3}$$

$$^3[RuL_3]^* \xrightarrow{k_{nr}} [RuL_3] \tag{4}$$

Bimolecular reactions competing with energy transfer to O_2 (*Eqn. 2*) might be physical deactivation of $^3[RuL_3]^*$ by O_2 (*i.e.*, oxygen-enhanced intersystem crossing, *Eqn. 5*) and electron transfer leading to the formation of superoxide anion and the oxidized form of the complex ($[RuL_3]^+$; *Eqn. 6*).

$$^3[RuL_3]^* + O_2 \xrightarrow{k_{dO_2}} [RuL_3] + O_2 \tag{5}$$

$$^3[RuL_3]^* + O_2 \xrightarrow{k_{ct}} [RuL_3]^+ + O_2^{\cdot -} \tag{6}$$

Taking into account *Reactions 1–6*, the quantum yield of singlet-oxygen production (Φ_Δ) is defined as [20],

$$\Phi_\Delta = \Phi_T \phi_{et} = \Phi_T \frac{k_{en}[O_2]}{k_r + k_{nr} + k_q[O_2]} \tag{7}$$

where
Φ_T is the quantum yield of triplet formation (intersystem crossing),
ϕ_{et}, the efficiency of energy transfer from $^3[RuL_3]^*$ to O_2,
k_{en}, the rate constant of energy transfer from $^3[RuL_3]^*$ to O_2, and
k_q, the sum of the rate constants of quenching of $^3[RuL_3]^*$ by O_2 ($= k_{en} + k_{dO_2} + k_{ct}$, *Eqns. 2, 5*, and *6*).

Φ_Δ can also be expressed as

$$\Phi_\Delta = \Phi_T \frac{k_q [O_2]}{k_r + k_{nr} + k_q [O_2]} \frac{k_{en}}{k_q} = \Phi_T P^T_{O_2} f^T_\Delta \tag{8}$$

where

$P^T_{O_2}$ ($= k_q[O_2]/\{k_r + k_{nr} + k_q[O_2]\}$) is the proportion of triplet excited states quenched by O_2 (also denoted as η in [13]), and

f^T_Δ ($= k_{en}/k_q$), the fraction of excited triplet states quenched by O_2 yielding $^1O_2$.

f^T_Δ is also denoted as S_Δ [21], and sometimes called '*efficiency of singlet-oxygen production*' or even '*quantum yield of singlet-oxygen production originating from the energy-transfer quenching of the excited triplet state by O_2*' [13]. This latter denomination should be avoided, as it introduces a confusion between f^T_Δ and Φ_Δ itself, all the more since the authors [13] add to the confusion by denoting f^T_Δ as Φ_Δ. The quantum yield of singlet-oxygen production Φ_Δ may depend considerably on the experimental conditions, in particular on the oxygen concentration, unless the product $k_q[O_2]$ is much larger than the sum $(k_r + k_{nr})$ in which case the triplet lifetime is long enough so that all triplet states are quenched by oxygen. The '*value of Φ_Δ corrected for 100% quenching of T_1*' [20] is in fact equal to the product $\Phi_T f^T_\Delta$.

$P^T_{O_2}$ and f^T_Δ are important parameters in the investigation of photosensitized reactions [20]. The proportion of excited triplet states quenched by oxygen, $P^T_{O_2}$, may be evaluated experimentally using the data obtained from the emission quenching experiments (*Table 2* and *Eqn. 9*).

$$P^T_{O_2} = \frac{k_q [O_2]}{k_r + k_{nr} + k_q [O_2]} = \tau k_q [O_2] = 1 - (\tau/\tau_0) = 1 - (I_0/I) \tag{9}$$

where $\tau = 1/(k_r + k_{nr} + k_q [O_2])$ and $\tau_0 = 1/(k_r + k_{nr})$, I_0 and I representing the steady-state emission intensities in the absence and in the presence of molecular oxygen, respectively.

The values of $P^T_{O_2}$ for [RuL$_3$] in air-saturated CD_3OD and D_2O solutions are listed in *Tables 3* (*Sect. 3.3*) and *4* (*Sect. 3.4*), respectively.

3.2. *Experimental Determination of Quantum Yields of Singlet-Oxygen Production.* Quantum yields of singlet-oxygen production by a sensitizer (Φ_Δ) may be experimentally determined by monitoring the weak monomolecular luminescence of singlet oxygen in the near-IR at 1270 nm (see *e.g.* [22–24]). Details of our method of analysis under monochromatic continuous excitation of the sensitizer have already been published [25–27]. The intensity of the electrical signal observed (S_e) is proportional to the quantum yield of $^1O_2$ luminescence (Φ_e), the latter depending on Φ_Δ (*Eqn. 10*).

$$\Phi_e = P_e/P_a = C S_e/P_a = \Phi_\Delta \frac{k_e}{k_d + k_t^{Sens} [Sens]} \tag{10}$$

where

P_e is the rate of photons emitted by $^1O_2$,

P_a, the rate of absorption of photons by the sensitizer,

C, the apparatus factor,

k_e, the rate constant of $^1O_2$ emission,
k_d, the rate constant of $^1O_2$ deactivation by the solvent ($k_d \gg k_e$), and
k_t^{Sens}, the total rate constant of $^1O_2$ quenching by the sensitizer itself (physical quenching and chemical reaction).

The singlet-oxygen luminescence signals of a solution containing the sensitizer under investigation (Sens = [RuL$_3$] in our case) (S_e) and of a solution containing a reference sensitizer (S_e^R) in the same solvent are alternatively measured, using identical absorbances at the wavelength(s) of excitation. Provided that singlet-oxygen quenching by the reference sensitizer is negligible compared to singlet-oxygen quenching by the solvent, the ratio of the luminescence signals, S_e/S_e^R (denoted as S) is given by

$$S = \frac{S_e}{S_e^R} = \frac{P_0}{P_0^R}\,\frac{\Phi_\Delta}{\Phi_\Delta^R}\,\frac{k_d}{k_d + k_t^{[RuL_3]}[[RuL_3]]} \qquad (11)$$

where P_0/P_0^R is the ratio of the incident photon rates (= 1, if [RuL$_3$] and reference are excited at the same wavelength) and
Φ_Δ^R, the quantum yield of $^1O_2$ production by the reference sensitizer.

If k_d and $k_t^{[RuL_3]}$ are known in the solvent used, Φ_Δ may be calculated from *Eqn. 11* by measuring the luminescence signals of [RuL$_3$] and reference solutions, as well as the corresponding incident photon rates [28]. If k/s([RuL$_3$],t) is not known, a Φ_Δ^{app} which has not been corrected for a potential $^1O_2$ quenching by the sensitizer itself (*Eqn. 12*) may be obtained. Φ_Δ and $k_t^{[RuL_3]}$ may then both be estimated by measuring the luminescence signals at two (or more) different absorbances.

$$\Phi_\Delta^{app} = \Phi_\Delta^R\, S\, \frac{P_0^R}{P_0} = \Phi_\Delta \frac{k_d}{k_d + k_t^{[RuL_3]}[[RuL_3]]} \qquad (12)$$

If the ratio S remains constant when the concentration of [RuL$_3$] varies, then the product $k_t^{[RuL_3]}[[RuL_3]]$ is negligible compared to k_d for the compound investigated under the applied experimental conditions, Φ_Δ^{app} remains constant within experimental error and, in the case where [RuL$_3$] and reference are excited at the same wavelengths, the ratio of the luminescence signals S is equal to the ratio of the quantum yields of singlet-oxygen production ($\Phi_\Delta/\Phi_\Delta^R$; *Eqn. 11*).

3.3. *Quantum Yields of Singlet-Oxygen Production by the [RuL$_3$] Complexes Investigated in CD$_3$OD.* The singlet-oxygen luminescence signals produced by 1*H*-phenalen-1-one as a reference sensitizer (λ_{ex} = 367 nm, $\Phi_\Delta^R = 0.97 \pm 0.04$) [26] and by the [RuL$_3$] complexes ($\lambda_{ex}$ = 367 nm and 437 nm) have been measured at 1270 nm using CD$_3$OD as a solvent (air-saturated solutions). The luminescence signals were stable under irradiation. Experiments were carried out at absorbances ranging from 0.17 to 1.65 at the excitation wavelengths. As molar absorption coefficients are smaller at 367 nm than at 437 nm (*Table 1*), concentrations were higher at the former wavelength. If, within experimental error, the ratio of the luminescence signals S (*Eqn. 11*) does not change with the concentration of [RuL$_3$], Φ_Δ is equal to the average experimental values of Φ_Δ^{app} (*Sect. 3.2, Eqn. 12*). As a consequence, only an upper limit of the value of the rate constant of singlet-oxygen quenching by the [RuL$_3$] complex may be calculated. This was the case, when exciting at 437 nm and sometimes also at 367 nm. Values of Φ_Δ, $k_t^{[RuL_3]}$, as well as examples of values of Φ_Δ^{app}, are given in *Table 3*.

As shown in *Table 3*, values of Φ_Δ vary considerably depending on the nature of the ligand of the [RuL$_3$] complex, ranging from 0.28 for $[Ru(bpz)_3]^{2+}$ to about 1.00 for $[Ru(dip)_3]^{2+}$ and $[Ru(dpds)_3]^{4-}$. The latter compounds substituted with aryl groups in the 4,7-positions have markedly longer excited-state lifetimes (*Table 2*) [9] [29] and are among the most efficient singlet-oxygen sensitizers. Adding sulfonate group to the dip ligand or a long hydrocarbon chain to the phen ligand does not affect Φ_Δ (values obtained for $[Ru(dip)_3]^{2+}$ and $[Ru(s2d)_3]^{4-}$, on the one hand, and for $[Ru(phen)_3]^{2+}$ and $[Ru(poda)_3]^{2+}$, on the other hand, are identical). Variations of Φ_Δ reflect directly the variations of $P_{O_2}^T$ (proportion of excited triplet states quenched by oxygen; *Eqn. 9*) since Φ_Δ is equal to $P_{O_2}^T$ within experimental error (*Table 3*). Consequently, both Φ_T and f_Δ^T are unity (*Eqn. 8*), and *the only quenching pathway of the excited [RuL$_3$] complexes by molecular oxygen in methanol is energy transfer leading to the production of singlet oxygen.* The rate constants of singlet-oxygen quenching by [RuL$_3$] are generally lower than 2×10^6 l mol^{-1} s^{-1}, except for the sulfonated compound ($[Ru(dpds)_3]^{4-}$).

There are only a few reports in the literature on the quantum yields of singlet-oxygen production by homoleptic Ru^{II} complexes in MeOH, and they concern $[Ru(bpy)_3]^{2+}$ [9] [30] [31]. Measurements were carried out by indirect methods using singlet-oxygen acceptors such as 2,3-dimethylbut-2-ene (tetramethylethylene), dibutyl sulfide, or 1,3-diphenylisobenzofuran. A value of Φ_Δ in oxygen-saturated MeOH (Φ_{Δ,O_2}) of 0.83 was reported from laser flash photolysis experiments with a standard deviation of ±20% [30].

Table 3. *Quantum Yields of Singlet-Oxygen Production* (Φ_Δ), *Proportion of Excited Triplet States Quenched by Molecular Oxygen* ($P_{O_2}^T$) *and Rate Constants of Singlet-Oxygen Quenching* ($k_t^{[RuL_3]}$) *for the [RuL$_3$] Complexes Investigated in Air-saturated CD$_3$OD*

[RuL$_3$]	[[RuL$_3$]] [mol l^{-1}]	Φ_Δ^{app} [a]) λ_{ex} = 367 nm	Φ_Δ [b])	$O_{O_2}^T$ [c])	$k_t^{[RuL_3]}$ [l mol^{-1} s^{-1}]
$[Ru(bpy)_3]^{2+}$	3.78×10^{-4} 4.28×10^{-5}	0.64 0.72	0.73	0.71 (0.73)	1.5(± 0.2) × 10^6
$[Ru(phen)_3]^{2+}$	2.26×10^{-4} 9.42×10^{-5}	0.52 0.54	0.54	0.58 (0.55)	≤ 1.8 × 10^6
$[Ru(bpz)_3]^{2+}$	4.25×10^{-4} 9.24×10^{-5}	0.23 0.27	0.28	0.35 (0.28)	2.1(± 0.2) × 10^6
$[Ru(dip)_3]^{2+}$	2.34×10^{-4} 2.63×10^{-5}	0.87 0.95	0.97	0.96 (0.95)	2.0(± 0.2) × 10^6
$[Ru(dpds)_3]^{4-}$	1.11×10^{-4} 4.94×10^{-5}	0.74 0.87	1.00	0.94 (0.96)	1.2(± 0.1) × 10^7
$[Ru(poda)_3]^{2+}$	2.34×10^{-4} 7.56×10^{-5}	0.53 0.55	0.54	[d]) (0.55)	≤ 1.7 × 10^6

[a]) $\Phi_\Delta^{app} = \Phi_\Delta^R$ S (*Eqn. 12*), reference sensitizer: 1*H*-phenalen-1-one, Φ_Δ^R = 0.97, λ_{ex}^R = 367 nm [26].

[b]) Standard deviation: ± 8%.

[c]) Calculated as $(1 - \tau/\tau_0)$; values in parenthesis calculated as the product $(k_q\tau[O_2])$; standard deviation: ± 5%.

[d]) Calculation from the relation $(1 - (\tau/\tau_0))$ was not possible due to the multiexponential emission decay in Ar-saturated solution (*Table 2, Sect. 2*).

A Φ_{Δ,O_2} of 0.86 may be estimated from the reported quantum yield of photooxidation of dibutyl sulfide [31]. Calculation of Φ_{Δ,O_2} from our results in air-saturated solutions (*Eqn. 13*) leads to a value of 0.93(±0.6) which is in rather good agreement with the published results taking into account the different experimental techniques used and the errors involved.

$$\Phi_{\Delta,O_2} = \Phi_{\Delta,air} ([O_2]_{O_2}/[O_2]_{air}) (\tau_{O_2}/\tau_{air}) \qquad (13)$$

Extrapolated values of the quantum yields of oxygen uptake at infinite concentrations of acceptor and oxygen, representing in fact the product $\Phi_T f_\Delta^T$, have been evaluated to be 0.86 or 0.95 for $[Ru(bpy)_3]^{2+}$ depending on the acceptor used and 0.75 for $[Ru(phen)_3]^{2+}$ [9] [32]. However, f_Δ^T [15] and Φ_T [33–36] values of unity have been published for $[Ru(bpy)_3]^{2+}$ in better agreement with our results. The identical values of Φ_Δ and $P_{O_2}^T$ observed for the series of $[RuL_3]$ complexes investigated in this work demonstrate that Ru^{II} complexes containing six-membered heterocyclic chelating ligands should have Φ_T values of unity as well. This result has been previously assumed by several authors although without direct experimental evidence [9] [37] [38].

3.4. *Determination of the Quantum Yields of Singlet-Oxygen Production by the $[RuL_3]$ Complexes Investigated in D_2O.* The singlet-oxygen luminescence signals produced by rose bengal as a reference sensitizer (λ_{ex} = 547 nm, $\Phi_\Delta^R = 0.75$ [39–41]) and by the Ru^{II} complexes (λ_{ex} = 437 nm) have been measured at 1270 nm in air-saturated D_2O. Under the

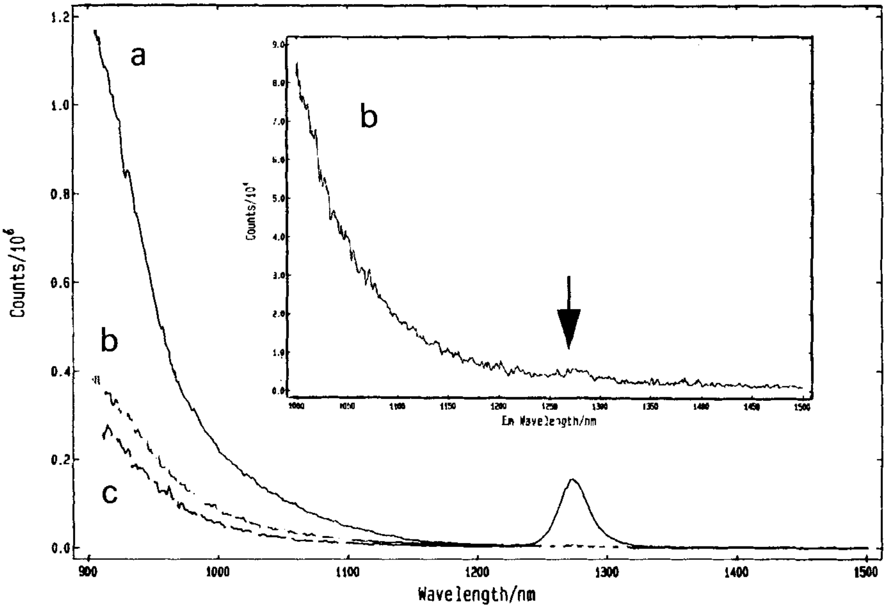


Figure. *Corrected emission spectra in the near-IR of aerated solutions of $[Ru(dip)_3]^{2+}$.*
a) In CD_3OD, *b*) in D_2O, and *c*) in H_2O (λ_{ex} = 461 nm, see *Exper. Part*); the band centered at 1270 nm corresponds to the emission of singlet oxygen.

experimental conditions used, quenching of singlet oxygen by [RuL_3] is negligible compared to deactivation by the solvent (concentrations lower than 6×10^{-5} mol l^{-1}, rate constant of singlet-oxygen deactivation in D_2O higher than in CD_3OD [42–44]). However, whereas the contribution of the emission tail of the [RuL_3] complexes to the luminescence signal at 1270 nm was negligible in CD_3OD, this was not the case in D_2O due to a shorter singlet-oxygen lifetime and, thus, a smaller luminescence signal in the latter solvent. The near-IR emission spectra of aerated solutions of $[Ru(dip)_3]^{2+}$ in CD_3OD, in D_2O and H_2O are given in the *Figure* for comparison.

The contribution of the emission from the [RuL_3] excited state (E) to the total signal measured at 1270 nm (S_m) was determined using NaN_3 as a singlet-oxygen quencher (Q). In a prior series of experiments, the rate constant of singlet-oxygen quenching by NaN_3 (k_Q) was determined by a *Stern-Volmer* analysis, using 1*H*-phenalen-1-one and rose bengal as sensitizers. The relationship between the ratio of the signals observed in the absence (S_e^0) and in the presence (S_e^Q) of quencher and the quencher concentration (*Eqn. 14*) was linear. A value of $5.0(\pm 0.4) \times 10^8$ l mol^{-1} s^{-1} was obtained for k_Q of NaN_3 in agreement with published values [45] [46].

$$S_e^0/S_e^Q = 1 + k_Q \tau_\Delta [Q] \tag{14}$$

where τ_Δ is the $^1O_2$ lifetime in the solvent used in the absence of Q (see *Exper. Part* for the determination of τ_Δ).

In the case of the [RuL_3] complexes investigated, the signals measured at 1270 nm (S_m^0 in the absence of Q or S_m^Q in its presence) are the sum of the singlet-oxygen luminescence signal (S_e^0 or S_e, resp.) and of the signal due to the emission from the [RuL_3] excited state (E; *Eqns. 15* and *16*).

$$S_m^0 = S_e^0 + E \tag{15}$$

$$S_m^Q = S_e^Q + E \tag{16}$$

Except for $[Ru(bpz)_3]^{2+}$, E remains constant in the range of NaN_3 concentrations used (3×10^{-5} mol l^{-1} to 2×10^{-4} mol l^{-1}), as no quenching of the emission of the [RuL_3] excited state by NaN_3 has been observed in SPC experiments. Since the values of k_Q, τ_Δ, and [Q] are known, the values of E and S_e^0 may be calculated from the measured signals S_m^0 and S_m^Q, by combining *Eqns. 14*, *15*, and *16*. Knowing S_e^0, Φ_Δ may then be determined relative to the reference (rose bengal) using *Eqn. 11* (where $k_t^{[RuL_3]^{2+}}[[RuL_3]^{2+}] \ll k_d$).

In the case of $[Ru(bpz)_3]^{2+}$, although no changes in the absorption spectra of $[Ru(bpz)_3]^{2+}$ could be observed, the excited-state emission was strongly quenched by NaN_3. This effect may be related to the presence of N-atoms which are not coordinated to the metal center in the bpz ligands. An efficient photoinduced proton transfer may occur between the excited complex and the hydrazoic acid, the predominant form of the N_3^- ion under the pD conditions used in this work (no buffer) [47]. Probably for a similar reason, the excited-state emission of $[Ru(bpz)_3]^{2+}$ was also quenched by DABCO (1,4-diazobicyclo[2.2.2]octane), another efficient inhibitor of singlet oxygen [48]. Therefore, we have determined the quantum yield of $^1O_2$ production by $[Ru(pbz)_3]^{2+}$ in D_2O using a different method. The signals in the near-IR have been measured using air-, Ar-, and N_2-saturated solutions. The singlet-oxygen luminescence signal in air-saturated solution

(S_e^0) has then be calculated using *Eqn. 17*, and Φ_Δ determined relative to the reference (rose bengal) as indicated above in the case of methanol.

$$S_e^0 = S_m^{air} - E_{air} = S_m^{air} - E_0(\tau_{air}/\tau_0) \quad (17)$$

where S_m^{air} is the total luminescence signal measured in air-saturated solution, E_{air}, the emission signal of $[Ru(bpz)_3]^{2+}$ excited state in air-saturated solution, and E_0, the emission signal of $[Ru(bpz)_3]^{2+}$ excited state measured in the absence of oxygen (Ar- or N_2-saturated solution).

Values of Φ_Δ and $P_{O_2}^T$ in air-saturated D_2O for the $[RuL_3]$ complexes investigated are given in *Table 4*. As in CD_3OD, values of Φ_Δ vary depending on the nature of the ligand of the $[RuL_3]$ complex from 0.18 for $[Ru(bpz)_3]^{2+}$ to 0.43 for $[Ru(dip)_3]^{2+}$ and $[Ru(dpds)_3]^{4-}$, and introduction of sulfonate groups to the dip ligand does not affect $P_{O_2}^T$ or Φ_Δ. However, Φ_Δ values are lower than in CD_3OD by a factor of 1.5 ($[Ru(bpz)_3]^{2+}$) to 3.3 ($[Ru(bpy)_3]^{2+}$). Moreover, in contrast to the results in CD_3OD, Φ_Δ is lower than $P_{O_2}^T$, except for $[Ru(bpz)_3]^{2+}$.

Singlet-oxygen production by $[Ru(bpy)_3]^{2+}$ and $[Ru(bpz)_3]^{2+}$ as well as by a series of heteroleptic Ru^{II}-diimine complexes of the form $[Ru(bpy)_{3-m-z}(bpm)_m(bpz)_z]^{2+}$ (bpm = 2,2′-bipyrimidine) in O_2-saturated D_2O has been investigated recently [13]. To our knowledge, no data are available for the other compounds investigated in this work. We have recalculated the values of Φ_{Δ,O_2} from the experimental data obtained by steady-state and time-resolved luminescence measurements in the near-IR reported by

Table 4. *Characteristic Parameters for Singlet-Oxygen Production in Air-Equilibrated D_2O and Driving Forces for the Electron-Transfer Reaction from the Triplet Excited State to Molecular Oxygen (ΔG_{CT}) for the [RuL_3] Complexes Investigated*

$[RuL_3]$	%E[a])	Φ_Δ[b])	$O_{O_2}^T$[c])	f_Δ^T[d]) (k_{en}/k_q)	k_{en} [l mol^{-1} s^{-1}]	E_0 $[RuL_3]^+/[RuL_3]^*$ [V][e])	ΔG_{CT}[h]) [kJ mol^{-1}]
$[Ru(bpy)_3]^{2+}$	58	0.22	0.46	0.48	1.6×10^9	−0.84 (NHE)	−54
$[Ru(phen)_3]^{2+}$	21	0.24	0.54	0.44	1.8×10^9	−0.87 (NHE)	−57
$[Ru(bpz)_3]^{2+}$	53	0.19	0.16	1.2	5.6×10^8	−0.17 (NHE)[f])	11
$[Ru(dip)_3]^{2+}$	27	0.42	0.79	0.53	1.7×10^9	−1.01 (NHE)	−70
$[Ru(dpds)_3]^{4-}$	27	0.43	0.78	0.55	1.6×10^9	[g])	[g])

[a]) Contribution of the emission from $[RuL_3]$ to the luminescence signal in the near IR.

[b]) Standard deviation: ± 10%, except for $[Ru(bpz)_3]^{2+}$ (± 15%).

[c]) Calculated as $k_q \tau [O_2]$.

[d]) $f_\Delta^T = \Phi_\Delta / P_{O_2}^T$, assuming $\Phi_T = 1$ (see text, *Sect. 2.4*).

[e]) Values in H_2O taken from [6] unless otherwise indicated.

[f]) Calculated from the value *vs. SCE* (−0.10 V) [52], relative to the value published for $[Ru(dip)_3]^{2+}$ [51].

[g]) Not determined.

[h]) $\Delta G_{CT} = -F[E_0(O_2/O_2^{-\cdot}) - E_0([RuL_3]^+/[RuL_3]^*)]$, with $E_0(O_2/O_2^{-\cdot}) = -0.284$ V (*vs.* NHE) [53] and F the *Faraday* constant.

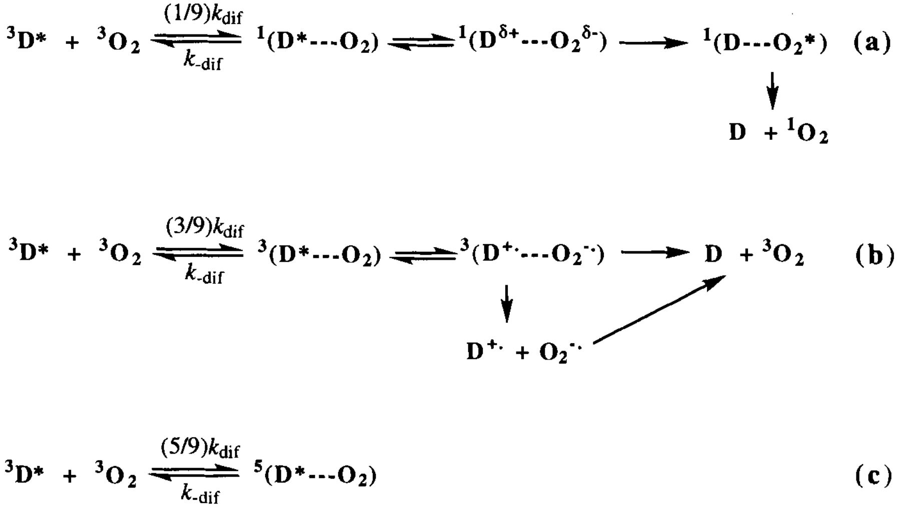
Mulazzani et al. [13] (as already mentioned in *Sect. 3.1*, these authors discuss actually f_Δ^T values denoting them as Φ_Δ): singlet-oxygen quantum yields relative to $[\mathrm{Ru(bpy)_3}]^{2+}$ are equal to the ratios of the corresponding luminescence signals ($\mathrm{L}_\mathrm{o}^\mathrm{x}/\mathrm{L}_\mathrm{o}^\mathrm{r}$). From these data and the absolute value for $[\mathrm{Ru(bpy)_3}]^{2+}$ determined by comparison with tetrasodium-tetrakis(4-sulfonatophenyl)porphine [13], we have recalculated a $\Phi_{\Delta,\mathrm{O_2}}$ of 0.40 for $[\mathrm{Ru(bpy)_3}]^{2+}$ and 0.52 for $[\mathrm{Ru(bpz)_3}]^{2+}$. In very good agreement with these results, $\Phi_{\Delta,\mathrm{O_2}}$ calculated from our values of Φ_Δ obtained in air-saturated solution (*Eqn. 13*) are 0.38 and 0.56, respectively.

The quantum yield of intersystem crossing of $[\mathrm{Ru(bpy)_3}]^{2+}$ in aqueous solution has been measured by laser flash photolysis techniques and found to be close or equal to unity [34] [36]. In the case of $[\mathrm{Ru(bpz)_3}]^{2+}$, Φ_Δ and $P_{\mathrm{O_2}}^\mathrm{T}$ in $\mathrm{D_2O}$ (as in $\mathrm{CD_3OD}$) are identical within experimental error (*Tables 3* and *4*), and, therefore, both Φ_T and f_Δ^T are equal to 1. Assuming that Φ_T in water is also unity for $[\mathrm{Ru(phen)_3}]^{2+}$, $[\mathrm{Ru(dip)_3}]^{2+}$, and $[\mathrm{Ru(dpds)_3}]^{4-}$, f_Δ^T ($= \Phi_\Delta/P_{\mathrm{O_2}}^\mathrm{T}$) varies from 0.44 to 0.55 for the $\mathrm{Ru^{II}}$ complexes investigated in this work, with the exception of $[\mathrm{Ru(bpz)_3}]^{2+}$ (*Table 4*). Therefore, except for $[\mathrm{Ru(bpz)_3}]^{2+}$, *energy transfer leading to the production of singlet oxygen is not the only pathway of quenching of the excited [RuL$_3$] complexes by molecular oxygen in water.* Values of f_Δ^T for $[\mathrm{Ru(bpy)_3}]^{2+}$ (0.5) and $[\mathrm{Ru(bpz)_3}]^{2+}$ (*ca.* 1) in $\mathrm{D_2O}$ are in good agreement with previously published results [13].

4. Discussion. – A remarkable solvent effect on the quenching of the $[\mathrm{RuL_3}]$ excited state by molecular oxygen is found, when the corresponding results in $\mathrm{CD_3OD}$ and $\mathrm{D_2O}$ (*Tables 2–4*) are compared. Main observations are as follows: *1*) In $\mathrm{D_2O}$, higher quenching rate constants (k_q) (despite higher solvent viscosity) but lower quantum yields of singlet-oxygen production (Φ_Δ) than in $\mathrm{CD_3OD}$ have been observed. A solvent dependence of k_q was already reported for $[\mathrm{Ru(bpy)_3}]^{2+}$, $[\mathrm{Ru(bpz)_3}]^{2+}$, and $[\mathrm{Ru(bpm)_3}]^{2+}$, but corresponding Φ_Δ values were not measured [12]. *2*) In $\mathrm{CD_3OD}$, quenching of the $[\mathrm{RuL_3}]$ triplet by molecular oxygen occurs exclusively through energy transfer to give singlet oxygen ($f_\Delta^\mathrm{T} = k_\mathrm{en}/k_\mathrm{q} = \Phi_\Delta/P_{\mathrm{O_2}}^\mathrm{T} = 1$), whereas f_Δ^T in $\mathrm{D_2O}$ is *ca.* 0.5 for the series of compounds investigated in this work, with the exception of $[\mathrm{Ru(bpz)_3}]^{2+}$ (*Table 4*). *3*) $[\mathrm{Ru(bpz)_3}]^{2+}$ appears as a particular case in both solvents: k_q is one order of magnitude lower compared to the other complexes, and, despite the fact that $[\mathrm{Ru(bpz)_3}]^{2+}$ has the lowest Φ_Δ in both solvents due to a lower efficiency of quenching of its excited state by oxygen, it is the only compound of the series for which the quenching process leads exclusively to the production of singlet oxygen in both methanol and water.

Energetics are one of the key parameters controlling the rate of excited-state quenching processes. Quenching of the sensitizer triplet state by oxygen *via* energy transfer to produce singlet oxygen (*Eqn. 2*) is thermodynamically allowed for $[\mathrm{RuL_3}]$ complexes, since $^3[\mathrm{RuL_3}]^*$ lies by *ca.* 2 eV above the corresponding ground state for all compounds, and the energy content of $\mathrm{O_2}(^1\Delta_\mathrm{g})$ is 0.98 eV higher than that of ground-state molecular oxygen [49]. However, electron transfer (*Eqn. 6*), if thermodynamically allowed, might compete with energy transfer. We have listed in *Table 4* the values of $E_0([\mathrm{RuL_3}]^+/^3[\mathrm{RuL_3}]^*)$ [6] and the corresponding driving forces for charge transfer from $^3[\mathrm{RuL_3}]^*$ to molecular oxygen (calculated as the free-energy changes for ion pair formation, ΔG_CT) [50]). The former parameter has been evaluated from the oxidation potential ($E_0([\mathrm{RuL_3}]^+/[\mathrm{RuL_3}])$) and the 0–0 transition energy of the corresponding $[\mathrm{RuL_3}]$ complex. Oxidation potentials of Ru^{II}-diimine complexes have been mostly measured in MeCN, but values in H_2O are available for $[Ru(bpy)_3]^{2+}$ [6] [51]. Therefore, relative values in this solvent may be calculated and used for comparative purposes [6] [13] [14] [52]. For solubility reasons, redox potentials could not be measured for $[Ru(poda)_3]^{2+}$ and $[Ru(dpds)_3]^{4-}$ in MeCN. However, it is likely that the corresponding values are close to those of $[Ru(phen)_3]^{2+}$ and $[Ru(dip)_3]^{2+}$, respectively, as it is expected that substituents in 4,7-positions will not affect significantly the ground-state energies. Among the complexes investigated in this work, $[Ru(bpz)_3]^{2+}$ is the most difficult to oxidize, and electron transfer from its excited triplet state to oxygen is endothermic (*Table 4*). On the contrary, charge-transfer energetics are largely favorable for all the other complexes with ΔG_{CT} values of −54 to −70 kJ mol^{-1}, compared to +11 kJ mol^{-1} for $[Ru(bpz)_3]^{2+}$.

Scheme



As mentioned above, energy transfer is the only mechanism for the quenching by molecular oxygen of the excited triplet of all $[RuL_3]$ complexes investigated in *methanol* ($f_\Delta^T = 1$), and the quenching rate constants k_q (*Table 3*) represent the experimental rate constants for energy transfer k_{en} (*Eqn. 2*). Quenching of excited states by oxygen in fluid solution occurs *via* a collisional mechanism, and spin-statistical factors for the encounter complex predict that the limiting value of k_{en} should be equal to one-ninth of the diffusion-controlled rate constant (k_{dif}) [54] [55] (*Scheme*, *Path a*). This rate constant, when oxygen is one of the reaction partners, has been evaluated to be 3.1×10^{10} l mol^{-1} s^{-1} in MeOH [56] and might be slightly lower in CD_3OD due to the higher solvent viscosity [57] [58]. Therefore, k_{en} values obtained experimentally in this solvent are relatively close to, or slightly less, than the predicted value of $k_{dif}/9$ (*ca.* 3×10^9 l mol^{-1} s^{-1}), *the exception being* $[Ru(bpz)_3]^{2+}$ *for which* k_{en} *is a hundred times lower than* k_{dif}. This significant ligand effect may be explained by the fact that charge-transfer interactions within the encounter complex (*Scheme*, *Path a*), which play an important role in energy-transfer processes by electron exchange (collisional mechanism) [54] [55] [59] [60], are not favorable in the case of $[Ru(bpz)_3]^{2+}$, the weakest reductant in the series. Some authors have proposed that, in case of a thermodynamically favored electron-transfer quenching, singlet oxygen might be formed by recombination of $[RuL_3]^+$ and $O_2^{-\cdot}$ ions [11]. However, such a mechanism should be discarded as it has been shown that quenching between $[Ru(bpy)_3]^{3+}$ and $O_2^{-\cdot}$ generated independently failed to produce singlet oxygen [61]. If electron transfer would occur, fast back transfer would lead to the ground-state species [13], and the overall process would be equivalent to oxygen-enhanced intersystem crossing (*Eqn. 5*) competing with singlet-oxygen production: such a process is obviously not taking place in MeOH.

With the exception of $[Ru(bpz)_3]^{2+}$, the fact that Φ_Δ is about half of $P_{O_2}^{T}$ in D_2O (*Table 4*) demonstrates that another reaction path competes with energy transfer for the quenching of $^3[RuL_3]^*$ by oxygen in D_2O. The diffusion-controlled rate constant in water may be estimated to be 1.8×10^{10} l mol^{-1} s^{-1}, taking into account the value measured in methanol and the relative solvent viscosities [56–58]. Although values of k_{en} (*Table 4*) are close to the predicted limit ($k_{dif}/9$) as in methanol, they are about half the corresponding k_q for the reducing complexes (*Table 2*). This could be the consequence of a more pronounced charge-transfer character of the encounter exciplex in water than in methanol: the existence of low-lying charge-transfer states might promote oxygen-enhanced intersystem crossing (*Scheme*, *Path b*) and account for the difference observed between k_{en} and k_q. A similar mechanism has been proposed in order to explain rate constants of quenching of triplet states of several aromatic compounds by oxygen greater than $k_{dif}/9$ [21] [55] and reduced quantum yields of singlet-oxygen production [62]. The magnitudes of k_q and f_Δ^T for several aromatic hydrocarbons and ketones have been found to be inversely correlated and to exhibit a pronounced sensitivity to the free energy change for charge transfer to molecular oxygen (ΔG_{CT}) [63] [64]. Complete electron transfer from $^3[RuL_3]^*$ to molecular oxygen might occur along the reaction path (*Scheme*, *Path b*); however, $[RuL_3]^+$ could not be detected in laser flash photolysis experiments [13] and, if complete electron transfer does occur, it is followed by fast recombination of the geminate ion pair within the solvent cage, as suggested previously [13]. In fact, oxygen-enhanced intersystem crossing (*Eqn. 5*) and electron transfer to form superoxide anion (*Eqn. 6*) belong the same quenching pathway (*Scheme*, *Path b*).

Solvents effects on k_q and f_Δ^T following a similar trend as observed in our case have been reported for substituted naphthalenes [63]: lower oxygen-quenching rate constants (k_q) and higher efficiencies of singlet-oxygen production (f_Δ^T) in a nonpolar solvent (cyclohexane) than in a polar one (MeCN), where charge-transfer interactions are favored. However, reported variations are much smaller than those observed between methanol and water in the case of the reducing $[RuL_3]$ complexes. Therefore, quenching of $^3[RuL_3]^*$ by molecular oxygen appears to be highly sensitive to the particular solvating properties of water. It should be noted that, in the case of $[Ru(bpz)_3]^{2+}$, the rate constant for energy transfer k_{en} ($= k_q$) is higher in D_2O than in CD_3OD (*Table 2*), in contrast to all other complexes, and is only *ca.* 30 times lower than k_{dif} in D_2O (compared to 100 times lower in CD_3OD). This indicates that solvent properties play also a significant role in the energy-transfer process itself.

Interestingly, in the series of compounds investigated in water by *Mulazzani et al.* [13], $[Ru(bpy)_3]^{2+}$ appears as the exception with f_Δ^T equal to 0.5, whereas for complexes of the form $[Ru(bpy)_{3-m-z}(bpm)_m(bpz)_z]^{2+}$, including $[Ru(bpz)_3]^{2+}$, triplet quenching occurs exclusively by energy transfer ($f_\Delta^T = 1$). For these latter compounds, the driving force for charge transfer is at least 30 kJ mol^{-1} less favorable than that for $[Ru(bpy)_3]^{2+}$ [13], the oxidation potential for the bipyrimidine ligand falling in between those for bpy and bpz. Combining results from [13] and from this work, we can conclude that there is a threshold in ΔG_{CT} which controls the quenching pathways of triplet excited states of Ru^{II}-diimine complexes by molecular oxygen in water.

Ru^{II} Complexes based on the 4,7-diphenyl-1,10-phenanthroline (dip) ligand present several advantages as singlet-oxygen sensitizers: they have high Φ_Δ values in polar organic solvents even in air-saturated solution, they are soluble in most polar protic and aprotic organic solvents (eventually by changing the counterion), they undergo neither photochemical nor secondary dark reactions, their rate constant of singlet-oxygen quenching (k_t^{Sens}) is low, and they can be excited in a wide wavelength range.

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Experimental Part

Chemicals. $[Ru(bpy)_3]Cl_2 \cdot 6\ H_2O$ and $[Ru(phen)_3]Cl_2 \cdot 6\ H_2O$ (*Aldrich*) were used as received. $[Ru(dip)_3Cl_2 \cdot 5\ H_2O \cdot 3$ HCl and $[Ru(bpz)_3]Cl_2 \cdot 3.5\ H_2O$ were prepared according to the method previously published for similar homoleptic Ru^{II} complexes [65]. $[Ru(poda)_3](AcO)_2 \cdot 1\ H_2O \cdot 3$ AcOH was synthesized as indicated in [66]. $Na_4[Ru(dpds)_3]Cl_2 \cdot 12\ H_2O$ was synthesized by refluxing $RuCl_3 \cdot n\ H_2O$ (*Aldrich*) with a 3.6 times excess of the bathophenanthroline disulfonic acid disodium salt trihydrate (*Fluka*) in a mixture of EtOH/H_2O (75% *v/v*) for 5 h under Ar. The crude product was filtered, dissolved in H_2O, and reprecipitated with EtOH; the colloid was centrifuged during 20 min at 4000 rpm, and the orange solid was collected by filtration and dried in a vacuum desiccator over P_2O_5.

Rose bengal and *1H*-phenalen-1-one (*Fluka, puriss.*) were used as reference sensitizers in CD_3OD and D_2O, respectively. *1H*-Phenalen-1-one was purified as indicated in [26]. CD_3OD (> 99.5% D, *Dr. Glaser*, Basel, Switzerland, 99.8% D, *MSD Isotopes, Merck*, or 99.5% D, *Janssen*) and D_2O (99.9% D, *Aldrich*, or 99.8% D, *CEA CE Saclay*, France) were used as solvents. NaN_3 (99%) and DABCO (1,4-diaza[2.2.2]bicyclooctane) were purchased from *Aldrich* and *Fluka*, resp., and dried overnight before use in a desiccator.

Absorption Spectra. Absorption spectra were recorded at r.t. on a *Perkin-Elmer Lambda-3* interfaced to a *DG 386SX16* computer or on a *Shimadzu UV-260* spectrophotometer. The molar absorption coefficients at different wavelengths are given in *Table 1*.

Quenching of the [RuL$_3$] Complexes Emission by Molecular Oxygen. The *Stern-Volmer* analysis of the steady-state [RuL$_3$] emission quenching by molecular oxygen was performed on a *Perkin-Elmer LS50* spectrofluorometer interfaced with an *IBM PS/55SX* computer for instrument control, data transfer, and processing. The [RuL$_3$] emission lifetimes were measured using the time-correlated single-photon counting (TC-SPC) technique on an *Edinburgh Analytical Instruments* (Edinburgh, UK) *FL900* spectrometer. The 337-nm line of a hypobaric N_2-filled discharge lamp, pulsed at 20.0 or 40.0 kHz (1.5 mm gap electrode), was used for excitation. The instrument was equipped with a *Peltier* cooled (−26°) *Hamamatsu R-955* red sensitive photomultiplier. A *COP 386SX20* computer was used for controlling the spectrometer and the multichannel analyzer, for collecting and analyzing data. The decay traces obtained were deconvoluted for the instrumental response and fitted to a single, double or triple exponential function using the nonlinear *Marquardt* algorithm included in the *Edinburgh Analytical Instruments* original software package. The reduced χ^2 weighed residuals and autocorrelation function were employed to estimate the quality of the fits. Temp. control (23.0 ± 0.2°) was provided by a *Haake D8-GH* circulator. Lifetime measurements were performed in air-saturated, Ar- or O_2-saturated solns. purged with the corresponding gas for at least 15 min before the measurements. Oxygen concentrations at 23° were calculated using the *Ostwald* or *Bunsen* solubility coefficients for each solvent [67]. The partial pressure of oxygen was calculated by substracting the vapor pressure of each solvent from the measured total pressure. The average atmospheric pressure in Madrid is 710 mm Hg. Calculations lead to values of *ca.* 1.68×10^{-3} mol l^{-1} and 2.5×10^{-4} mol l^{-1} in air-saturated methanol and water, respectively.

Singlet Oxygen Luminescence Measurements. Our equipment based on a continuous monochromatic excitation of the sensitizer for the measurements of the $^1O_2$ luminescence at 1270 nm has already been described [26] [27]. Measurements for the determination of the Φ_Δ of the [RuL_3] complexes were carried out at two different wavelengths of irradiation (λ_{ex} = 3 7 nm and 437 nm) in CD_3OD and at 437 nm in D_2O. A Xe/Hg lamp (1 kW, *Osram, Müller*) and a monochromator (*ISA Jobin-Yvon B204*, 6-nm bandwidth) were used for the irradiation. Because of the short lifetimes of $^1O_2$ (τ_Δ) in CH_3OH and H_2O and the small rate constants of $^1O_2$ luminescence (k_e) [68] [69], the perdeuterated solvents (where τ_Δ are much longer [42]) were used in order to increase the intensity of the luminescence signals. 1*H*-Phenalen-1-one [26] and rose bengal [38–40] were used as reference sensitizers in CD_3OD and D_2O, respectively. Absorbances of the Ru^{II} complexes and of the reference sensitizers at corresponding λ_{ex} were identical for a given series of measurements. Equivalent 1-cm fluorescence cells were used for the luminescence experiments. Series of measurements alternating between reference and sample were carried out, the irradiation time being 3 min for each sample. The results are the average of at least two series of measurements. In the case where different λ_{ex} were used for the reference and the compound investigated, the incident radiant powers (F_0, mW) were measured using a thermopile (*Laser Instrumentation*, model *154*), and the ratios of the incident photon rates ($P_0/P_0^R = (F_0\lambda_{ex})/(F_0^R\lambda_{ex}^R)$) were calculated. The incident radiant powers were *ca.* 8.5 mW at 367 nm, 5.5 mW at 437 nm, and 4.5 mW at 547 nm.

Singlet-oxygen luminescence measurements for the *Stern-Volmer* analysis of the quenching of singlet oxygen by NaN_3 in D_2O were made with solns. of identical absorbance (*ca.* 1.5) at the wavelength of excitation of the sensitizer ([RuL_3], 1*H*-phenalen-1-one, or rose bengal). The sample solns. were prepared from stock solns. of the sensitizer and of the quencher. Three different concentrations of NaN_3 were used between 3.0×10^{-5} and 1.3×10^{-4} mol l^{-1}. Luminescence signals were stable during irradiation time (3 min), except for rose bengal, in which case slightly decreasing signals were observed and values at the beginning of the irradiation time were used.

Singlet-oxygen lifetimes (τ_Δ) in CD_3OD and D_2O were determined on a time-resolved luminescence detection apparatus [70]. τ_Δ in CD_3OD varies between 250 and 270 (±5) μs depending on the origin of the solvent, and τ_Δ in D_2O was found equal to 62(±2) μs, in agreement with previously measured values [41–43]. It should be noted that singlet-oxygen luminescence signals are smaller in D_2O than in CD_3OD due the $^1O_2$ lifetime difference and, as a consequence, experimental errors are larger in D_2O.

Near-IR luminescence spectra generated by excitation of [$Ru(dip)_3$]Cl_2 in CD_3OD, D_2O, and H_2O were recorded on a *FS900* spectrometer by *Edinburgh Analytical Instruments* (Edinburgh, UK). The apparatus was equipped with a 450-W Xe excitation lamp and the near-IR luminescence option, an excitation monochromator (300 mm focal length, f/No. 4.2, linear dispersion 1.8 nm/mm, 1800 g/mm holographic grating, 250 nm optimized), an emission monochromator (300 mm focal length, f/No. 4.2, linear dispersion 5.4 nm/mm, 600 g/mm ruled grating, 1 μm blazed) and a highly sensitive liquid-N_2-cooled Ge detector (*North Coast EO817L* with muon filter). The signal from the Ge detector was processed using a lock-in technique. These measurements were made with an additional 850-nm cut-off filter in the emission channel in order to eliminate second order effects and minimize stray light. The curves shown (*Fig.*) are corrected for filter and instrument characteristics.

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