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Size effects on the luminescence quenching of Tb^{3+} by Ru(II) tetraammines with alkyl *trans*-phosphane ligands

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Abstract

The luminescence quenching of $^*Tb^{3+}$ by tetraammines of Ru(II) complexes with phosphane ligands of the type *trans*-$[Ru(NH_3)_4(P(OR)_3)_2](PF_6)_2$ with $R = CH_3, C_2H_5, {}^iC_3H_7, C_4H_9, {}^tC_4H_9$, is studied in aqueous solution. The results indicate that the quenching process occurs by collisional energy transfer with possible formation of a photoactive triplet ligand-field excited state of the Ru(II) complex which undergoes NH_3 photoaquation. The observed luminescence quenching rate constants are within the range 1.1 ($R = {}^tC_4H_9$) to 3.3 ($R = CH_3$) $\times 10^6\ M^{-1}\ s^{-1}$ depending on the type of alkyl chain in the phosphane ligand. Bulky substituents on the P ligand reduce the rate of luminescence quenching by inducing steric factors and consequently increasing the pair contact distance for collisional energy transfer. For *n*-alkyl phosphane ligands, this size effect on the quenching rate constant is well correlated with the ligand cone angle θ. © 1997 Elsevier Science S.A.

Keywords: Terbium ion; Ruthenium complex; Luminescence quenching; Size effects

1. Introduction

Photo-induced energy and electron transfer in transition metal complexes has been a topic of constant investigation in recent decades, with several applications in the fields of photocatalysis, solar energy conversion, and molecular electronics [1–4]. Most of the progress in this field, specially in supramolecular photochemistry, has been supported by important advances in synthetic methods.

Synthesis of new complexes of Ru(II) based on photolabilization reactions of ligands have been recently proposed as alternative routes to thermal reaction [5]. Tetraammines of Ru(II) with *trans*-phosphane ligands are of particular interest in photochemistry studies because these complexes do not usually show an overlap between ligand-field (LF) and charge-transfer (CT) bands, allowing a selective electronic excitation to form LF excited states. Furthermore, the *trans*-$[Ru(NH_3)_4(P(OR)_3)_2]^{2+}$ ions do not emit when irradiated on their LF absorption bands. Photoreactivity towards ligand substitution in this class of Ru complexes has been ascribed to the presence of a lower energy triplet excited state with ligand-field (^3LF) character [5,6].

In this paper, the luminescence quenching of the Tb^{3+} ($^5D_4$) excited state by a series of Ru(II) complexes with *trans*-phosphane ligands having different alkyl chains is investigated in terms of two possible reaction pathways: photo-induced electron transfer or energy transfer between the terbium ion and the ruthenium complex. The effect of the quencher molecular structure on the kinetics of the collisional quenching is analyzed. Applications in photosensitized ligand substitution are also discussed.

2. Experimental details and methods

The synthesis and characterization of the *trans*-$[Ru(NH_3)_4(P(OR)_3)_2](PF_6)_2$ complexes with $R = CH_3$, C_2H_5, ${}^iC_3H_7$, C_4H_9, ${}^tC_4H_9$, have been described previously [7]. Ether, ethanol, and acetone (Aldrich) were distilled under reduced pressure before use. All other materials were reagent grade and were used without further purification. Ruthenium trichloride ($RuCl_3 \cdot 3H_2O$) was the starting material for the synthesis of the ruthenium complexes. Terbium chloride hexahydrate (Alfa-Ventron) was dried in a desiccator. Trifluoracetic acid (Merck, spectroscopic grade) was used as purchased. All aqueous solutions were prepared using doubly distilled water.

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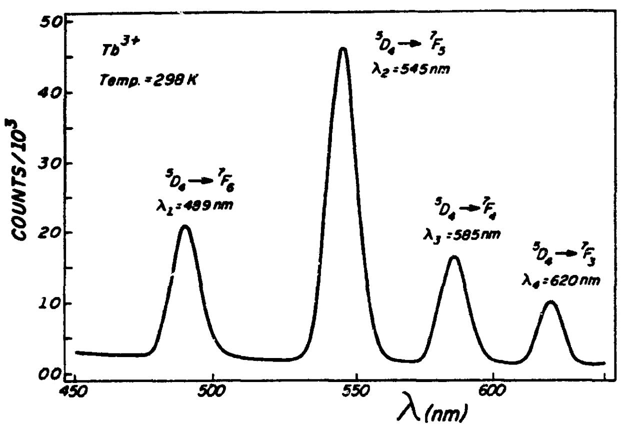

Fig. 1. Corrected steady-state emission spectrum of 1 mM Tb^{3+} in aqueous solution containing 1 mM trifluoracetic acid/dimethyl ketone (1:1) at 298 K.

Half-wave oxidation potentials of the complexes in an aqueous solution of 1 mM trifluoracetic acid/dimethyl ketone (1:1) at 298 K were determined by cyclic voltammetry using a PARC model 170 electrochemical system. The electrochemical cell was of the three-electrode type formed by a saturated calomel electrode (SCE), a platinum wire (auxiliary electrode) and a working glassy-carbon electrode. The solvent mixture used in the electrochemical measurements was the same as that employed with the samples of ruthenium complexes in the presence of terbium chloride in the luminescence quenching experiments. The pH of the samples was determined using a digital Corning pH meter model 130.

UV–visible absorption measurements were performed at room temperature with a HP 8451-A spectrophotometer. The analysis of the electronic absorption spectra of these complexes based on a d^6 low-spin ion of D_{4h} symmetry has been published previously [5b].

Corrected steady-state emission spectra of the 1 mM Tb^{3+} solutions were recorded at 298 K using an Edinburgh CD 900 photon counting spectrofluorimeter. Fig. 1 shows the emission spectra of the Tb^{3+} working solution with the characteristic four emission bands. Relative luminescence intensities were calculated from the integration of the most intense emission band centered at 545 nm. The luminescence lifetime τ_0 of the Tb^{3+} ($^5D_4$) in solution was determined using a CD 900 Edinburgh microsecond time-resolved phosphorescence spectrometer.

3. Results and discussion

The luminescence lifetime τ_0 of the Tb^{3+} ($^5D_4$) measured in the working solution was 434 ± 5 μs, which is quite close to the reported value of 480 s in pure water at 298 K [8].

In the presence of *trans*-$[Ru(NH_3)_4(P(OR)_3)_2]^{2+}$ ions with R = CH_3, C_2H_5, $^{i}C_3H_7$, C_4H_9, $^{t}C_4H_9$, the luminescence intensity of $^{*}Tb^{3+}$ decreases as shown in Fig. 2. The intensity ratio in the absence and presence of added complex follows a linear Stern–Volmer relationship:

$$I_0/I = 1 + k_q\tau_0[Q] \qquad (1)$$

and the slope of I_0/I vs. [Q] depends on the quencher complex used (see Fig. 3).

A good linear fit to Eq. (1) has been obtained for all the above systems, the quenching rate constants (k_q) are in the range 1.1 (R = $^{t}C_4H_9$) to 3.3 (R = CH_3) × 10^6 M^{-1} s^{-1}, as reported in Table 1. These rate constants are one order of

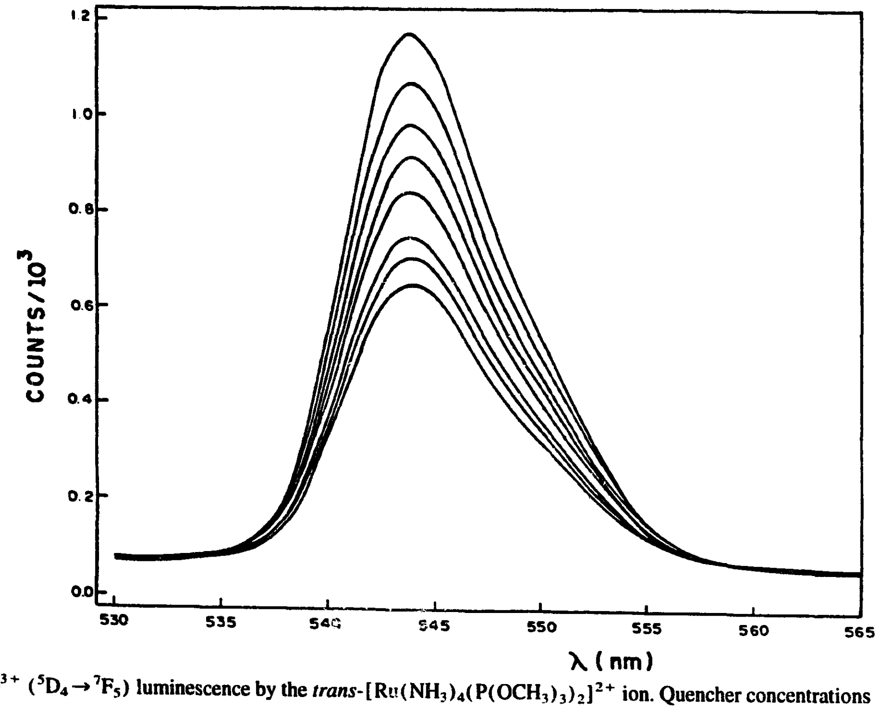

Fig. 2. Quenching of Tb^{3+} ($^5D_4 \rightarrow {}^7F_5$) luminescence by the *trans*-$[Ru(NH_3)_4(P(OCH_3)_3)_2]^{2+}$ ion. Quencher concentrations between 0.14 and 2.2 mM.

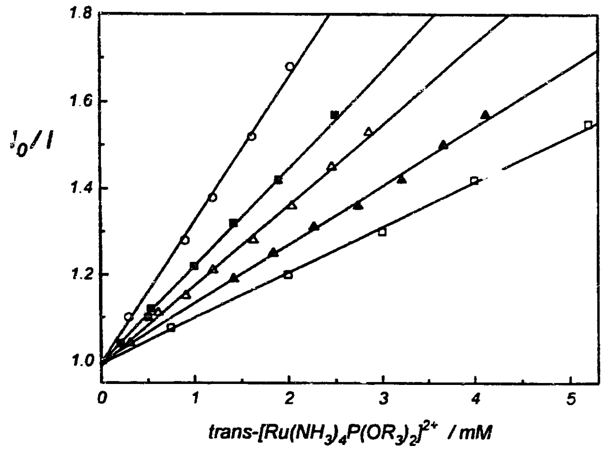

Fig. 3. Plots for the luminescence quenching of Tb^{3+} *trans*-$[Ru(NH_3)_4(P(OR)_3)_2]^{2+}$ complex ions (R = ○, CH_3; ■, C_2H_5; △, $^iC_3H_7$; ▲, C_4H_9; □, $^iC_4H_9$).

Table 1
Quenching rate constant k_q of $*Tb^{3+}$ by *trans*-$[Ru(NH_3)_4(P(OR)_3)_2]^{2+}$ as a function of the half-wave potential (Ru(III)/Ru(II)) and cone angle θ at 298 K

$P(OR)_3$	k_q (10^6 M^{-1} s^{-1})	$E_{1/2}$ (V vs. SCE)	θ (deg)[a]
CH_3	3.30	0.73	107
C_2H_5	2.25	0.70	109
$^iC_3H_7$	1.86	0.68	130
C_4H_9	1.36	0.66	112
$^iC_4H_9$	1.07	0.64	172

[a] From [18].

magnitude smaller than the k_q values reported for the quenching of $*Eu^{3+}$ by $Ru(NH_3)_6^{2+}$ via reductive electron transfer [9]. The quenching of $*Tb^{3+}$ by these Ru(II) complexes via electron transfer can be described by

$$*Tb^{3+} + Ru(II) \xrightarrow{k_q} Ru(III) + Tb^{2+} \quad (2)$$

with a standard free energy change $\Delta D^\circ = E_{1/2}(Ru(III)/Ru(II)) - E_{1/2}(Tb^{3+}/Tb^{2+}) - E_{0,0}$. The electronic energy $E_{0,0}$ of $*Tb^{3+}$ corresponds approximately to 2.52 eV, and the polarographic $E_{1/2}(Tb^{3+}/Tb^{2+})$ in aqueous solution is − 1.85 V (vs. SCE) [10]. Among the systems studied here, the highest driving force corresponds to the reactant donor with $R = {}^iC_4H_9$ and $E_{1/2}(Ru(III)/Ru(II)) = 0.64$ V for which $\Delta G^\circ = -0.03$ eV; for larger $E_{1/2}(Ru(III)/Ru(II))$ values, the forward electron-transfer reaction as given by Eq. (1) becomes an endoergonic process.

However, the observed decrease in k_q with $E_{1/2}(Ru(III)/Ru(II))$ is the reverse of the expected behavior for a photo-induced electron transfer if the transfer distance remains the same for all quenchers. For the title complexes, the sizes of the $P(OR)_3$ ligands are not equal and therefore the radius of the coordination sphere will change appreciably from one complex to another. The larger alkyl substituents R in the phosphane ligand will induce a greater steric factor, which will affect the close-contact distance d of the reactants. Accordingly [11], the rate constant of electron transfer decreases exponentially with d.

The rate constants for energy transfer by exchange interaction, according to the Dexter theory, are also a function of d:

$$k_{ET} = \frac{4\pi^2}{h}\exp[-d/L]\int_0^\infty E_D(\bar{\nu})\epsilon_A(\bar{\nu})d\bar{\nu} \quad (3)$$

where L is an effective average orbital radius for the initial and final electronic states of the donor and acceptor, and E_D and ϵ_A are the normalized emission spectra of the donor and the normalized molar extinction of the acceptor as a function of wavenumber, respectively [12]. Eq. (3) also predicts a linear relationship between ln k_q and d if quenching occurs by collisional energy transfer.

Although, owing to the heavy atom effect of the metal ion, the electronic states cannot be defined rigorously as singlet and triplet [13], an electronic energy transfer reaction can be assumed corresponding to

$$*Tb^{3+}(^5D_4) + Ru(II)(^1A_1) \xrightarrow{k_q} *Ru(II)(^3LF) + Tb^{3+}(^7F_n) \quad (4)$$

forming predominantly the triplet LF excited state of the ruthenium complex, in agreement with Wigner's spin rule [12].

These results, despite pointing out the relevance of the size of R in reducing the quenching rate constant of $*Tb^{3+}$, do not allow a definition concerning the nature of the process itself. Both photo-induced electron-transfer and collisional energy-transfer processes depend on a close approach of the two reacting partners and electronic interaction between the donor and acceptor orbitals. The ligand size effect on the quenching rate has been discussed previously [14–17].

However, if the quenching process occurs by collisional energy transfer with formation of $*Ru(II)$ (^3LF), then photosensitized aquation of the complex with terbium ions should be observed. Irradiation of the aqueous solution containing these Ru complexes with 313 nm light leads to the selective photoaquation of the NH_3 ligands [5b]:

$$[Ru(NH_3)_4(P(OR)_3)_2]^{2+} \xrightarrow{h\nu} *[Ru(NH_3)_4(P(OR)_3)_2]^{2+}$$

$$*[Ru(NH_3)_4(P(OR)_3)_2]^{2+} + H_2O \rightarrow [Ru(NH_3)_3(H_2O)P(OR)_3)_2]^{2+} + NH_3 \quad (5)$$

This photoreaction is clean and easily monitored through pH measurements. The $^1A_{2g}$ state initially formed is converted by intersystem crossing to the photoactive $^3A_{2g}$ LF excited state.

Photolysis experiments in the presence of 1 mM Tb^{3+} and *trans*-$[Ru(NH_3)_4(P(OCH_3)_3)_2]^{2+}$ with irradiation at 450 ± 10 nm forming $*Tb^{3+}$ ($^5D_4$) clearly indicate the presence of free NH_3 in the solution. In 5 min of sample irradia-

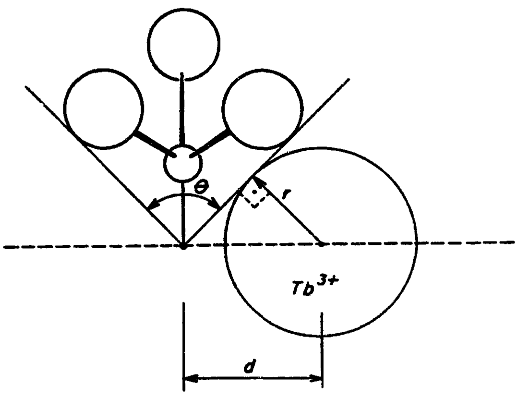

Fig. 4. Geometric scheme relating the cone angle θ of the ligand and the close-contact distance d.

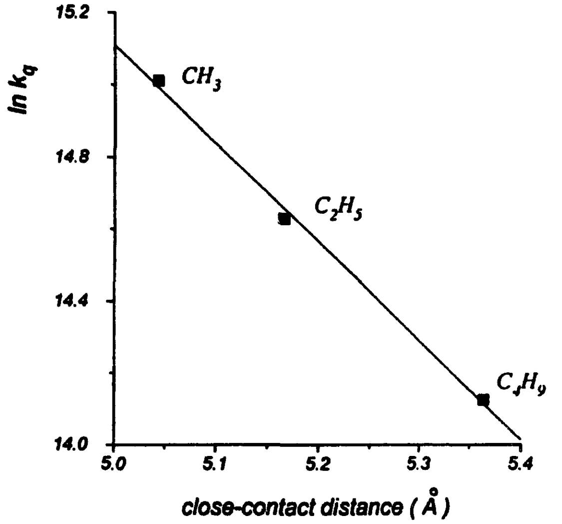

Fig. 5. Plot of the quenching rate constants as a function of the close-contact distance d for n-alkyl phosphane ligands.

tion, the measured change in pH (from an initial pH of 2.67 to a final pH of 2.82) indicated a 6% product conversion of the original solution at room temperature. Conversely, solutions containing the same complex but without Tb^{3+} when irradiated under the same conditions do not exhibit NH_3 photoaquation.

These results strongly suggest that the quenching process of $^{*}Tb^{3+}$ by $trans$-$[Ru(NH_3)_4(P(OR)_3)_2]^{2+}$ ions is better explained by an energy transfer pathway than by electron transfer.

The steric factor and size effect promoted by the alkyl substituents on the quenching rate constant are correlated to the phosphane cone angle θ [18]. Fig. 4 gives a pictorial representation of the relationship between θ and the close-contact distance d of the reactants. The analytical equation relating θ and d considering a hydrated Tb^{3+} ion with a radius of about 3 Å is given by

$$d=\frac{3}{\sin\left(90-\frac{\theta}{2}\right)} \tag{6}$$

The increase in θ leads to larger contact distance d and hence a reduction of k_{ET}, as predicted by Eq. (3). In fact, the measured k_q values decrease with θ as reported in Table 1. If k_q is proportional to k_{ET}, then a plot of ln k_q vs. d should be linear, and this trend is observed for n-alkyl derivatives (see Fig. 5). The linear relationship does not depend on the assumed radius of the hydrated terbium ion, as it is a multiplicative factor only. For R = $^{i}C_3H_7$ and $^{t}C_4H_9$, the phosphane cone angles are higher and d as estimated by Eq. (6) becomes larger than the radius of the coordination sphere of the phosphane ligand; therefore, the close-contact distance d cannot be evaluated properly using this geometrical model.

4. Conclusions

The luminescence quenching of $^{*}Tb^{3+}$ by tetraammines of Ru(II) complexes with $trans$-phosphane ligands seems to occur by collisional energy transfer with possible formation of a triplet LF excited state of the ruthenium complex. The luminescence quenching rate constant is of the order of 10^6 M^{-1} s^{-1} and depends on the type of alkyl chain on the phosphane ligand. Bulky substituents on the P ligand reduce the rate of luminescence quenching by inducing steric factors and consequently increasing the pair contact distance for collisional energy transfer.

Acknowledgements

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