

# Luminescence Studies of the *trans*-[Cr–Cyclam(CN)<sub>2</sub>]ClO<sub>4</sub> (Cyclam = 1,4,7,11-Tetraazacyclotetradecane) Complex: Its Luminescence Spectra in Several Solvents and the Concentration Dependence of Its Luminescence Lifetime

László Vincze,<sup>1,2</sup> Flórián Sándor,<sup>1</sup> Judit Pém,<sup>1</sup> and Gyöngyi Bosnyák<sup>1</sup>

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The luminescence lifetime ( $\tau_{\text{lum}}$ ) and the luminescence spectra of the title complex (**I**) were determined in eight solvents. We found that in spite of former assumptions, the  $\tau_{\text{lum}}$  of **I** depends on the concentration of the complex. We determined the self-quenching ( $k_Q$ ) and Stern–Volmer ( $K_{\text{SV}}$ ) constants, and the relative values of luminescence quantum yields in eight solvents. There was no measurable self-quenching in 1,2-ethanediol and *N,N*-dimethylformamide; dynamic self-quenching was found (the concentration dependence of  $\tau_{\text{lum}}$  and  $\phi_{\text{lum}}$  was the same) in *N,N*-dimethylacetamide, dimethylsulfoxide, water, propylene–carbonate, and pyridine. In acetonitrile we found both dynamic and static self-quenching based on the different concentration dependence of  $\tau_{\text{lum}}$  and  $\phi_{\text{lum}}$  of **I**;  $K_{\text{SV}}$  and the association constant of **I** in acetonitrile were computed.

**KEY WORDS:** Cr–cyclam; luminescence spectra; luminescence lifetime; self-quenching; Stern–Volmer constants.

## INTRODUCTION

The luminescence spectra of the *trans*-[Cr–cyclam(CN)<sub>2</sub>]ClO<sub>4</sub> complex at room temperature have received little attention in solution so far [1]. The luminescence lifetime of the *trans*-[Cr(cyclam)(CN)<sub>2</sub>]ClO<sub>4</sub> complex has been measured by several authors [1–5] but either the concentration dependence of the luminescence lifetime was not studied [2–4] or no significant concentration dependence was found [1,5]. In the case of the similar *trans*-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>](OTS)<sub>3</sub> complex, our experiments [6] excluded the possibility of concentration dependence of the luminescence lifetime higher than the experimental errors so it was a surprise when in aqueous solutions we found that the luminescence lifetime of the

*trans*-[Cr(cyclam)(CN)<sub>2</sub>]ClO<sub>4</sub> complex slightly but certainly depended on the concentration of the complex. Our objective was to take the luminescence spectra of the *trans*-[Cr(cyclam)(CN)<sub>2</sub>]ClO<sub>4</sub> complex in several solvents and to study at the optimum wavelengths the dependences of the luminescence lifetimes on concentration.

## EXPERIMENTAL

### Instruments and Computations

The UV–Vis spectra were recorded by an M-40 UV–Vis spectrophotometer (Carl Zeiss, Jena).

The luminescence spectra were determined with an LS50 luminescence spectrophotometer (Perkin–Elmer) and also based on the transients generated by flashes of a Brilliant laser (Quantel). The transients were recorded

<sup>1</sup> Department of General and Inorganic Chemistry, University of Veszprém, P.O. Box 158, 8201 Veszprém, Hungary.

<sup>2</sup> To whom correspondence should be addressed.

between 600 and 800 nm. The output of the laser was followed, and its change was less than  $\pm 5\%$ .

The luminescence lifetime of the complex was studied by the laser flash photolysis instrument assembled at our department. The instrument includes the Brilliant laser, an Applied Photophysics kinetic spectrometer, a PM 3320A Phillips data-storing oscilloscope, and an IBM-compatible PC for instrument control and information storage. The normal emission wavelength of the Brilliant laser is 1064 nm and that wavelength was modified to 355 nm with a frequency-tripler system. The characteristic data of the laser pulses are  $1.6 \times 10^{17}$  photons, emitted at 355 nm (90 mJ), and a fwhm of 4.2 ns. The software which controls the instrument was developed at our department [7]. Further details are described elsewhere [8].

All measurements (UV–Vis and luminescence spectra, flash photolysis transients) were evaluated with the program Excel 5.0.

Luminescence lifetimes were computed from transients recorded at about 715 nm, where the highest peak of the luminescence spectra occurred. The time spans of transients used were at least three times longer than the lifetime concerned. Each lifetime was the average of three or four measurements, and each measurement included the evaluation of 8–20 transients.

## Chemicals

$\text{CrCl}_3 \cdot 3\text{THF}$  and cyclam were purchased from Aldrich; their purities were 99 and 98%, respectively. Millipore Q water and Aldrich solvents of HPLC quality [dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), pyridine, acetonitrile, 1,2-ethanediol, tetrahydrofuran (THF)] were used. Chemicals were used without further purification.

## Preparation of *trans*-[Cr–Cyclam(CN)<sub>2</sub>]ClO<sub>4</sub> and Samples

*trans*-[Cr–cyclam(CN)<sub>2</sub>]ClO<sub>4</sub> was prepared according to the literature [3]. The quality was checked by UV–Vis spectrophotometry ( $\epsilon_{330 \text{ nm}}$  and  $\epsilon_{420 \text{ nm}} \geq 62 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $\epsilon_{370 \text{ nm}} \leq 15 \text{ M}^{-1} \text{ cm}^{-1}$  conditions should be met) and by IR spectra. The required quality was achieved by two recrystallizations. The elemental analysis data (calculated) were as follows: Cr, 12.73; (12.88); C, 35.81 (35.69); H, 6.27 (5.99); N, 20.88 (20.81).

Solutions were freshly prepared, their concentrations were  $1 \times 10^{-4}$ – $2 \times 10^{-3} \text{ M}$ , depending on the solubilities. Samples were not deoxygenated, since, according to the literature [6] the presence or absence of oxygen has

no measurable effect on the  $\tau_{\text{lum}}$  or on the spectra of the complex.

## RESULTS AND DISCUSSION

### Luminescence Spectra in Solutions at Ambient Temperature

The luminescence spectra were obtained by LS50 fluorescence spectrophotometer and by the laser system as well: the steady-state luminescence spectra were closely reproduced in point-to-point by flash excitation spectra. The long lifetime ( $10^2 \mu\text{s}$ ) and low luminescence quantum yield ( $\approx 10^{-3}$  [9]) caused problems due to the low luminescence intensity; the detection of luminescence required such high attenuation that the Raman scattering of the laser pulse on the solvent molecules became detectable. There were two Raman peaks, at 600 and at 850 nm, but at the luminescence peak (715 nm) the Raman scattering was minimal. Both the luminescence spectra and the luminescence lifetimes were evaluated after the total decay of the Raman scattering.

The luminescence spectra taken in different solvents were practically identical, except in 1,2-ethanediol, where a blue shift of approximately 10 nm was found (Fig. 1). The luminescence lifetimes were determined by taking the luminescence transients between 710 and 715 nm.

### Luminescence Lifetimes

The luminescence lifetimes of the complex taken in different solvents are summarized in Table I. The measured lifetimes were calculated to zero complex concentration. The luminescence lifetimes of the complex depended on the concentration in the majority of the applied solvents. Only in DMF and 1,2-ethanediol was the concentration dependence unmeasurable. The self-quenching rate constants and the Stern–Volmer constants are also shown in Table I. It can be seen that in five solvents the Stern–Volmer constants are around  $10^2 \text{ M}^{-1}$ , but in acetonitrile the Stern–Volmer constant was about 90 times higher than in the other solvents.

In water, DMA, DMSO, propylene–carbonate, and pyridine, we assumed dynamic quenching based on the facts that the  $\tau_{\text{lum}}$  and the luminescence quantum yields changed in parallel (Fig. 2). In case of dynamic quenching the excited complex can lose its excess energy by colliding with a ground-state complex. Ground-state complex is abundantly available, because in the irradiated volume, only 4% of the complexes will be excited, while 96% of them remain in the ground state. It can be shown by the

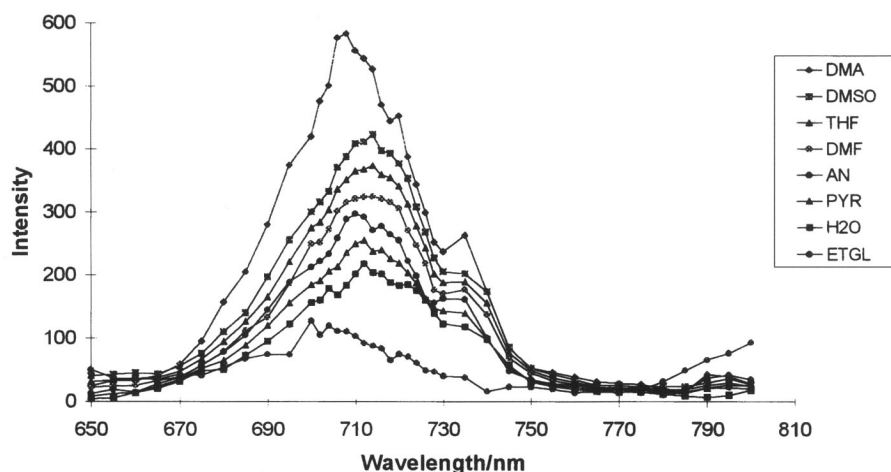


Fig. 1. Luminescence spectra of the *trans*-[Cr-cyclam(CN)<sub>2</sub>]ClO<sub>4</sub> complex.

following short calculations: the number of excited-state ( $N_{exc}$ ) and ground-state ( $N_{ground}$ ) complexes can be given by Eq. (1):

$$\frac{N_{exc}}{N_{ground}} = \frac{N_{exc}}{N_0 - N_{exc}} \quad (1)$$

where  $N_{exc} \cong N_{pulse} (1 - 10^{-\epsilon cd}) = N_{pulse} * 2.3\epsilon cd$ , and  $N_0 = VcN_A$ , so

$$\alpha = \frac{2.3N_{pulse}\epsilon cd}{VcN_A - 2.3N_{pulse}\epsilon cd} \quad (2)$$

$N_{pulse} = 1.6 \times 10^{17}$  photons,  $\epsilon_{355} = 24 M^{-1} cm^{-1}$ ,  $d = 1$  cm, and the cross section of the laser beam is  $0.385 cm^2$ , so the irradiated volume ( $V$ ) is  $3.85 \times 10^{-4} dm^3$ . With these data  $\alpha$  is equal to approximately 4%.

On the other hand, in acetonitrile both dynamic and static quenching can be assumed, since the concentration

dependence of  $\tau_{lum}$  and the luminescence quantum yields was different (Fig. 3, Table II). The static self-quenching means dimer formation ( $I_2$ ), therefore on the abscissa in Fig. 3 the free complex concentration is plotted, not the total analytical concentration of it. The reciprocal  $\tau_{lum}$  is a linear function of the concentration, showing the effect of the dynamic quenching. The slope gives the Stern–Volmer constant, which is equal to  $9.0 \times 10^3 M^{-1}$  in acetonitrile. The reciprocal luminescence quantum yield is not a linear function of the concentration and increases faster than the reciprocal  $\tau_{lum}$ , showing clearly the presence of the static quenching as well. In this case  $\phi_0/\phi_{lum}$  can be written [10] as

$$\frac{\phi_0}{\phi_{lum}} = (1 + K_m[I]) \times (1 + K_{sv}[I]) \quad (3)$$

where  $[I]$  is the free complex concentration;  $K_m$  is the

Table I. Stern–Volmer and Quenching Constants in Several Solvents ( $t = 20^\circ C$ ): Luminescence Lifetimes Were Calculated to Zero Concentration of the Complex<sup>a</sup>

| No. | Solvent           | $K_{sv} (M^{-1})$ | $k_Q (10^6 M^{-1} s^{-1})$ | $\tau_0 (\mu s)$ |
|-----|-------------------|-------------------|----------------------------|------------------|
| 1   | 1,2-Ethandiol     | 0                 | 0                          | 175              |
| 2   | DMF               | 0                 | 0                          | 34.1             |
| 3   | DMA               | 50                | 1.02                       | 59.4             |
| 4   | DMSO              | 96                | 0.55                       | 43.6             |
| 5   | Water             | 86                | 0.25                       | 339              |
| 6   | PrCO <sub>3</sub> | 151               | 0.44                       | 340              |
| 7   | Pyridine          | 180               | 17.3                       | 10.0             |
| 8   | Acetonitrile      | $9.0 \times 10^3$ | 59.5                       | 120              |

<sup>a</sup> We tried to prepare solutions of the complex by using solvents methanol, ethanol, propanols, butanols, propylamine, butylamines, 2-cyanopyridine, 2-methoxypyridine, and pyrimidine, but the complex was not soluble in them.

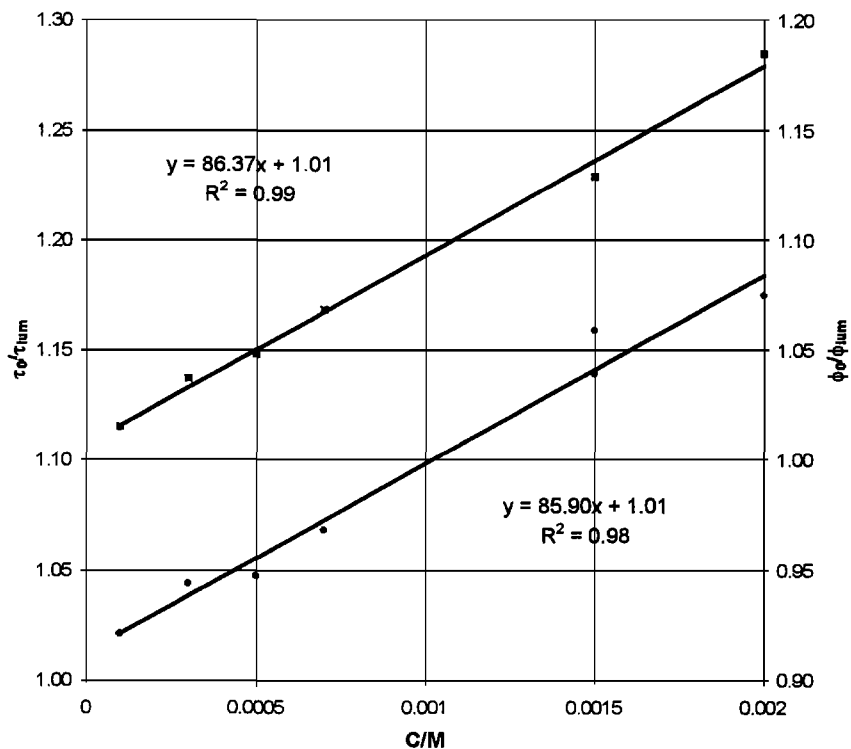


Fig. 2. Stern–Volmer plot for  $\tau_0/\tau$  (●) and  $\phi_0/\phi$  (■) of the complex in water.

association constant, multiplied by  $\epsilon_{12}/\epsilon_1$  [10]; and  $K_{SV}$  is the Stern–Volmer constant, calculated from  $\phi_{lum}$ ;

The optimum values of  $K_m$  and  $K_{SV}$  were  $8.9 \times 10^3$  and  $9.6 \times 10^3 M^{-1}$ , respectively. The values of  $K_{SV}$

calculated from  $\tau_{lum}$  and  $\phi_{lum}$  are equal within the estimated experimental error.

We expected to find similar results in pyridine as well because of the lone pair on the pyridine–nitrogen,

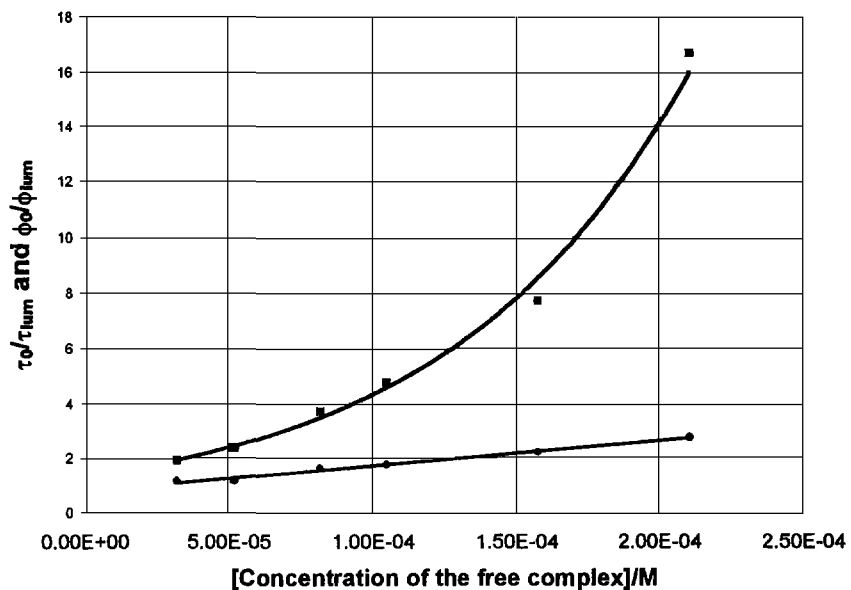
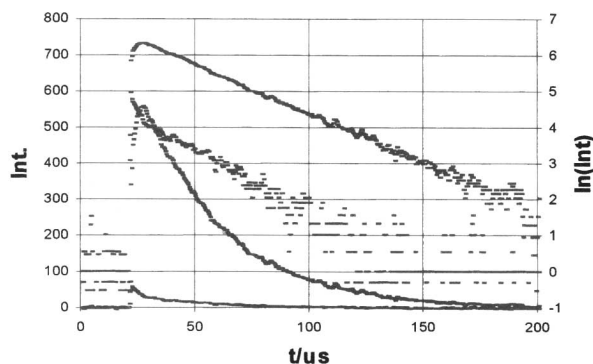


Fig. 3. Stern–Volmer plot for  $\tau_0/\tau$  (●) and  $\phi_0/\phi$  (■) of the complex in acetonitrile.



**Fig. 4.** Comparison of transients' dependence on pulse energy. Upper transient and linearized data, 90 mJ; lower transient and linearized data, 5 mJ.

but according to the experiences the acetonitrile can have a much stronger mutual effect with the *trans*-[Cr(cyclam)-(CN)<sub>2</sub>]ClO<sub>4</sub> than the pyridine has.

It is noteworthy from the point of view of science history that, earlier, the concentration dependence of the luminescence lifetime was not noticed because the laser used had only a 5-mJ output and the obtained fluorescence was so weak that the experimental errors were about equal to the changes caused by self-quenching. As we found, the experimental errors of lifetime determination were about 7–10% at a 5-mJ laser output and about 1–2% when the output exceeds 90 mJ. This means that in aqueous solutions 20–30 and 3–6  $\mu$ s are the respective absolute errors. The effect of different outputs is demonstrated in Fig. 4.

#### ACKNOWLEDGMENTS

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**Table II.** Relative Luminescence Quantum Yields (Related to Luminescence Quantum Yield of Water at  $c \approx 0$  mM) of the Complex in Several Solvents ( $t = 20^\circ\text{C}$ )

| No. | Solvent             | Range of $c$ (mM) | $\Phi_{\text{lum,rel}}$ |
|-----|---------------------|-------------------|-------------------------|
| 1   | 1,2-Ethanediol      | 0.05–0.6          | 1.1                     |
| 2   | DMF                 | 0.3–2.0           | 0.8                     |
| 3   | DMA                 | 0.1–0.5           | 1.1–1.2                 |
| 4   | DMSO                | 0.05–1.0          | 1.0–1.1                 |
| 5   | Water               | 0.1–2.0           | 1.0–1.2                 |
| 6   | Propylene-carbonate | 0.1–1.0           | 1.0–1.1                 |
| 7   | Pyridine            | 0.1–0.3           | 0.9–1.0                 |
| 8   | Acetonitrile        | 0.05              | 0.52                    |
| 9   | Acetonitrile        | 0.1               | 0.42                    |
| 10  | Acetonitrile        | 0.2               | 0.27                    |
| 11  | Acetonitrile        | 0.3               | 0.21                    |
| 12  | Acetonitrile        | 0.6               | 0.13                    |
| 13  | Acetonitrile        | 1.0               | 0.06                    |

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