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Flash photolysis studies of the *trans*-[Cr-cyclam(CN)$_2$]ClO$_4$ (cyclam = 1,4,7,11-tetraaza-cyclotetradecane) complex

Part 1. Elucidation of its luminescence lifetime's special solvent dependence; its luminescence spectra in several solvents

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Abstract

The luminescence lifetime (τ_{lum}) and the luminescence spectra of the title complex (I) were determined in eight and six solvents, respectively. The results were studied and interpreted with seven different solvent-effect parameters (Z, E_T, DN, AN, acidity, basicity, Kamlet–Taft parameters), and it was found that the solvent dependence of τ_{lum} can be described satisfactorily by the Kamlet–Taft parameters only. Furthermore, τ_{lum} of I demonstrated very clearly that the proper modeling of the solvent effect requires a vector → scalar type function.

Comparing our recent results with the formerly determined luminescence lifetimes of the similar *trans*-[Cr cyclam(NH$_3$)$_2$]$^{3+}$ complex ion (where the one-dimensional τ_{lum} vs. DN plot gave excellent correlation), the problem discussed was why the one-dimensional solvent-effect parameters have been useful so many times. © 1997 Elsevier Science S.A.

Keywords: Cr-cyclam; Solvent effect; Luminescence lifetime; Kamlet–Taft equation

1. Introduction

The luminescence spectra of the *trans*-[Cr-cyclam(CN)$_2$]ClO$_4$ complex at room temperature have been published in aqueous solution only [1], and its luminescence lifetime (τ_{lum}) was measured in H$_2$O, D$_2$O and DMSO [1,2]. Whereas the solvent dependence of τ_{lum} *trans*-[Cr-cyclam(NH$_3$)$_2$](OTS)$_3$ was studied in detail [3], the interpretation of that for *trans*-[Cr-cyclam(CN)$_2$]ClO$_4$ has been scarce [4]. Since we wish to deal with the detailed study of the *trans*-[Cr-cyclam(CN)$_2$]ClO$_4$ complex, our aim was to study the effect of the above-mentioned factors.

2. Experimental

2.1. *Instruments and computations*

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

The luminescence spectra were determined both with an LS50 luminescence spectrophotometer (Perkin–Elmer), and based on the transients generated by flashes of a Brilliant laser (Quantel). The transients were recorded between 600 and 800 nm. The output of the laser was followed, and its change was less than ±5%.

The luminescence lifetime of the complex was studied by the laser flash photolysis instrument assembled in our Department. The instrument includes the Brilliant laser, an Applied Photophysics kinetic spectrometer, PM 3320A Phillips data-storing oscilloscope, 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 pulses are: 1.6×10^{17} photons emitted at 355 nm (90 mJ), FWHM is 4.2 ns. The software which controls the instrument was developed at the Department [5]. Further details are described elsewhere [6].

All measurements (UV–Vis and luminescence spectra, flash photolysis transients) were evaluated with EXCEL 4.0.

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

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2.2. *Chemicals*

$CrCl_3 \cdot 3THF$ and cyclam were purchased from Aldrich, their purity was 99 and 98%, respectively. Millipore Q water and Aldrich solvents HPLC quality (dimethylsulfoxide (DMSO), *N,N*-dimethyl-formamide (DMF), *N,N*-dimethyl-acetamide (DMA), pyridine, acetonitrile, 1,2-ethanediol, tetrahydrofuran (THF)) were used. Chemicals were used without further purification.

2.3. *Preparation of trans-[Cr-cyclam(CN)$_2$]ClO$_4$ and samples*

Trans-[Cr-cyclam(CN)$_2$]ClO$_4$ was prepared according to the literature [7]. The quality was checked by UV–Vis spectrophotometry ($\epsilon_{330\,nm}$ and $\epsilon_{420\,nm} \geq 62$ M^{-1} cm^{-1}, $\epsilon_{370\,nm} \leq 15$ M^{-1} cm^{-1} conditions should be met) and by IR spectra. The required quality was achieved by two recrystallizations. The elemental analysis data (calculated): 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 4×10^{-4} to 5×10^{-3} M, depending on solubilities. Samples were not deoxygenated, since, according to the literature [3] the presence or absence of oxygen has no effect on the τ_{lum} value or on the spectra of the complex.

We tried to prepare solutions with methanol, ethanol, propanol, butanol, propylamine, butylamine, 2-cyanopyridine, 2-methoxypyridine, pyrimidine (purchased from Aldrich) as well, but the complex did not dissolve in these solvents.

3. Results

3.1. *Luminescence spectra in solutions at ambient temperature*

The luminescence spectra can be obtained by a LS50 fluorescence spectrophotometer and by the laser system as well: the steady-state luminescence spectra were closely reproduced point-to point by flash excitation spectra. The long lifetime (10^2 μs) and low luminescence quantum yield ($\approx 10^{-3}$ [8]) caused problems due to the low luminescence intensity: the detection of luminescence required so high an 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 perfect decay of 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).

3.2. *Luminescence lifetimes*

The luminescence lifetimes of the complex taken in different solvents are summarized in Table 1. The results were in an interesting contradiction to those of the *trans*-[Cr cyclam(NH$_3$)$_2$](OTS)$_3$ complex, where in organic solvents the luminescence lifetimes were higher, and the quenching rate constants were lower than in water [3,7]. For the cyano complex, τ_{lum} was especially low in pyridine and in acetonitrile. The causes are interpreted in Section 4.

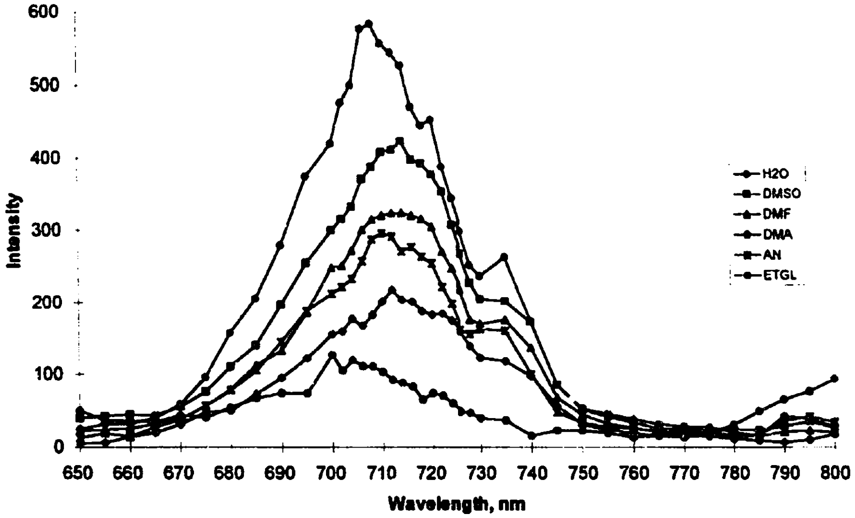

Fig. 1. Luminescence spectra of the *trans*-[Cr cyclam(CN)$_2$]ClO$_4$ complex in different solvents.

Table 1
Luminescence lifetime of *trans*-[Cr cyclam L_2]$^{n+}$ complexes in different solvents. t = 20°C

No.	Solvent	Luminescence lifetime (μs)	
		t-[Cr-cyclam($CN)_2$]ClO_4	t-[Cr-cyclam($NH_3)_2$]OTS_3
1	water	332	57.3
2	1,2-ethane-diol	175	
3	THF	59.3	
4	DMA	56.6	
5	acetonitrile	45.4	
6	DMSO	36.6	135
7	DMF	34.1	114
8	pyridine	9.6	

4. Discussion

In the earlier studied *trans*-[Cr cyclam($NH_3)_2$]($OTS)_3$ complex, a good correlation was found between measured luminescence lifetimes (τ_{lum}) or quenching rate constants (k) and donor number (DN) or acceptor number (AN) of the solvents used [3]. Thus, we sought similar connections in the beginning. We investigated the correlation between the quenching rate constants and the parameters DN, AN, Z, E_T [9], acidity and basicity [10], but the correlation with none of them was satisfactory (Table 2). The correlation really existed between k and the above-mentioned parameters, but that was a loose connection because k obviously depended on other factors as well.

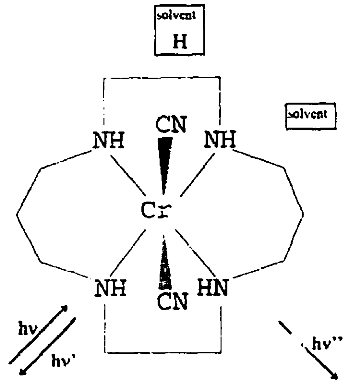

Fig. 2. Possibility of H-bonding of the *trans*-[Cr cyclam($CN)_2$]ClO_4 complex.

This multiparameter dependence can be understood from the structure of the *trans*-[Cr cyclam($CN)_2$]ClO_4 complex (Fig. 2), since the complex has a special double character: it can form hydrogen bonds in two ways. The equatorial N–H groups are electron pair acceptors and proton donors, whereas the axial CN ligands are electron pair donors and proton acceptors, so they can form hydrogen bonds of opposite directions and different effects. There are arguments against the H-bond forming abilities of equatorial N–H groups [2], but these arguments are negated by our findings and also by Scaiano et al. [11]. Scaiano et al. found that even the hydrogen of the C–H group can form a H-bond-like connection when its partner is the soft π-electrons of an aza-group.

Thus, it can be expected that for the proper characterization of solvent effects at least two parameters will be needed, as Drago stressed in his paper "The role of one parameter plots in a two parameter world" [12]. While the simple combination of AN and DN was not satisfactory, the extended equation of Kamlet and Taft worked well [13]:

$$\log k_i = \log k_0 + a\alpha_i + b\beta_i + s\pi_i^* + h\xi_i$$

where i is the ith solvent, α_i characterizes the proton donor ability of the solvent ($\rightarrow$DN), β_i characterizes the proton acceptor ability of the solvent ($\rightarrow$AN), π_i* is the ability to polarize or to be polarized ($\rightarrow n$, μ or/and ϵ), and ξ_i is the coordinate covalency.

Results and the optimum parameters can be seen in Fig. 3 and they are in accordance with the assumption that luminescence quenching constants are significantly affected by hydrogen bonds (a and b coefficients), but not only by them.

Table 2
Correlation between quenching rate constants (τ^{-1} in Table 1) and solvent parameters

No.	Solvent	DN	AN	Z	E_T	$d\nu_D$	Acidity	Basicity
1	H_2O	18	54.8	89.6	63.1		1	1
2	1,2-ethane-diol	20	48	85.1	56.3		0.78	0.84
3	THF	20	8	58.8	37.4	90	0.17	0.67
4	DMA	27.8	13.6	66.9	43.7	113	0.27	0.97
5	acetonitrile	14.1	18.9	71.3	46	49	0.37	0.86
6	DMSO	29.8	19.3	70.2	45	141	0.34	1.08
7	DMF	27	16	68.5	43.8	107	0.3	0.93
8	pyridine	33.1	14.2	64	40.2	168	0.24	0.96
R^2		0.452	0.659	0.632	0.692	0.51	0.818	0.01

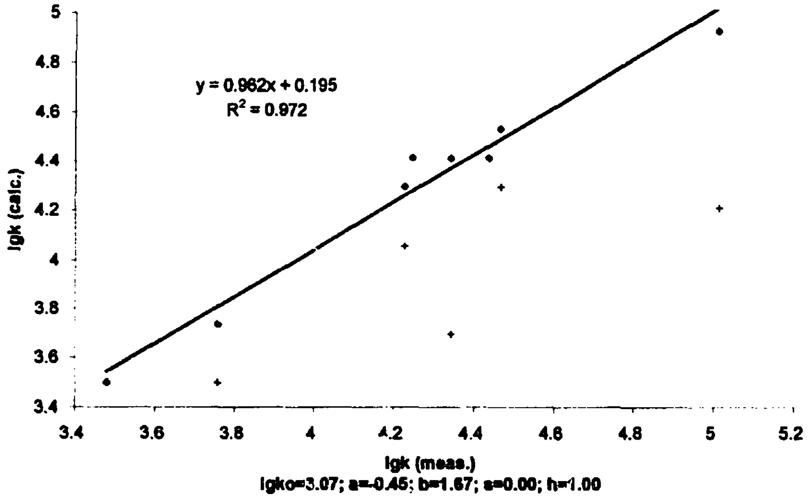

Fig. 3. Correlation of the measured and calculated log *k* on the basis of the extended Kamlet–Taft equation.

Taking into account *a* and *b* only would mean neglecting the coordinate covalency (ξ) that reflects the covalent contribution of some special functional groups (e.g. oxygen of sp^3 hybridization, hard lone pair of aromatic nitrogen, etc.) to the solvent effect. The points signed by crosses show the correlation without taking into account the coordinate covalency. The significantly increasing correlation suggests that the coordinate covalency proposed by Kamlet and Taft has physical meaning, and what is more, the coordinate covalency was responsible for the low luminescence lifetime of the *trans*-[Cr cyclam(CN)$_2$]ClO$_4$ complex in pyridine and acetonitrile.

Drago's proposal explains, and all our failed trials (when we tried to describe the solvent effect by only one parameter) stress, the fact that the former trials [4] were bound to fail as well. It is very interesting why the scalar description in the case of the similar *trans*-[Cr cyclam(NH$_3$)$_2$](OTS)$_3$ complex was successful. It was possible because of the special circumstance that this complex can form a hydrogen bond of one direction only, furthermore the four applied solvents did not show large differences in their coordinate covalency parameter ($-0.20<\xi<0.20$).

The salient point of optimum Kamlet–Taft parameters is that the *a* value computed is lower than zero and this strange value does have a physical meaning: formation of a solvent → complex H-bond instead of decreasing the stability and lifetime of excited state increases them. Kamlet and Taft mentioned this possibility [13]. The effect can be interpreted by the assumption that electron density increased by excitation to the direction of CN ligands (due to their high ligand field strength) is decreased by H-bond via the lone pairs of CN ligands, thus decreasing the driving force of the excited state decay.

5. Conclusions

The luminescence of the *trans*-[Cr cyclam(CN)$_2$]ClO$_4$ complex and the solvents selected together offer an excellent model to demonstrate the complexity of the solvent effect. For example it can be clearly seen that to describe the phenomena vector → scalar type τ(solvent) functions are needed. The objective of further studies is to extend the investigations to solvents containing oxygen of sp^3 hybridization or nitrogen in the aromatic ring.

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