

Solvent Effect on the Emission Lifetime and its Quantum Yield of $[(\text{Mo}^{\text{VI}}_6\text{Cl}_8)\text{Cl}_6]^{2-}$

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(Received December 6, 1988)

Abstract

Emission lifetime (τ_{em}) and quantum yield (ϕ_{em}) of the hexanuclear molybdenum cluster, $[(\text{Mo}^{\text{VI}}_6\text{Cl}_8)\text{Cl}_6]^{2-}$, have been measured in six solvent media: CH_3CN (180 μs , 0.19), dimethylformamide (81.9 μs , 0.099), CH_3OH (30.0 μs , 0.038), 6 M HCl (13.5 μs , 0.017), 2 M HCl (5.0 μs , 0.0054), 0.2 M HCl (3.7 μs , 0.0025). From these data, it is concluded that radiative rate constants (k_r) are similar (6.8×10^2 – $1.27 \times 10^3 \text{ s}^{-1}$) in different solvents and non-radiative rate constants (k_{nr}) are significantly different (2.70×10^5 – $4.51 \times 10^3 \text{ s}^{-1}$). Solvent effect on the vibrational decay processes and on the excited state energy levels cannot account for the difference in k_{nr} . Solvent assisted photo-dissociation of coordinated chloride ion(s) is most likely responsible for the solvent effect.

Introduction

Since the discovery of the strong red emission of $[(\text{Mo}^{\text{VI}}_6\text{Cl}_8)\text{Cl}_6]^{2-}$ both in solution and in the crystalline state [1], various studies have been carried out to elucidate the excited state properties of this cluster ion and its derivatives [1–11]. An interesting feature of the emission properties of $[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]^{2-}$ in solution is remarkable solvent dependence of the emission lifetime; e.g. 20 μs in 6 M HCl and 180 μs in acetonitrile. This fact was noticed earlier [1], but no detailed study has been made so far for clarifying the origin of the solvent effect. We have now examined the emission lifetime and the quantum yield of

$[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]^{2-}$ in a variety of solvents in order to find a more general view of the solvent effect.

Experimental

Materials

$\text{K}_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]$ and $[(\text{C}_2\text{H}_5)_4\text{N}]_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]$ were prepared as described elsewhere [4, 12]. Commercial special grade hydrochloric acid was treated with a small amount of $\text{NH}_2\text{OH}\cdot\text{HCl}$ to remove Cl_2 and then distilled. The concentration was determined by the titration with a standard NaOH solution. Lithium perchlorate was recrystallized once from water and dried *in vacuo* at 200 °C. Special grade reagent of lithium chloride monohydrate was used as received. Organic solvents for fluoroanalytical use were used without further purification.

Photochemical Measurements

The emission intensity was measured with a SPEX Fluorolog 2. Calibration was made by the internal program. The hexamolybdenum cluster showed an emission peak at 765 nm with an identical half-width regardless of the solvents on irradiation of ultraviolet light. Quantum yield of the emission (ϕ_{em}) was determined from the relative intensity of the emission peak on irradiation at 340 nm. The reported quantum yield in acetonitrile, 0.19 [1], as determined with the irradiation wavelength at 436 nm, was used as a standard. It was assumed that ϕ_{em} does not depend significantly on the wavelength of incident light. This assumption is reasonable since the ratio of emission intensities on the irradiation at 340 nm and at 436 nm was close to the ratio of the absorbance at these two wavelengths. Since the absorbance at 340 nm and the emission peak intensity did not show strictly linear correlation, a calibration curve was prepared for the determination of ϕ_{em} using an acetonitrile solution of $[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]^{2-}$.

The emission lifetime (τ_{em}) was measured by irradiating at 337 nm with an N_2 laser (JS-1000L of

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TABLE 1. Photophysical data of $[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]^{2-}$ in various solvents

Solvent	τ_{em} (μs)	ϕ_{em}	k_{r} (s)	k_{nr} (s)	k_{nc} (s) ^a
$\text{CH}_3\text{CN}^{\text{b}}$	180.0	0.19	1.05×10^3	4.51×10^3	0
DMF	81.9	0.099	1.21×10^3	1.10×10^4	6.5×10^3
CH_3OH	30.0	0.038	1.27×10^3	3.21×10^4	2.8×10^4
6 M HCl	13.5	0.017	1.26×10^3	7.28×10^4	6.7×10^4
2 M HCl	5.0	0.0054	1.08×10^3	1.99×10^5	2.0×10^5
0.6 M HCl ^c	3.7	0.0025	6.8×10^2	2.70×10^5	2.7×10^5

^aSee text. ^b τ_{em} values in the presence of 0.1 M electrolyte in acetonitrile: $151 \pm 2 \mu\text{s}$ (NaClO_4), 150 ± 3 (HCl), 152 ± 2 ($(\text{C}_2\text{H}_5)_4\text{NCl}$), 146 ± 2 ($(\text{C}_2\text{H}_5)_4\text{NClO}_4$), 145 ± 2 ($n\text{-Bu}_4\text{NClO}_4$). In air saturated solutions all electrolytes give τ_{em} values of *c.* $11.5 \mu\text{s}$. ^c τ_{em} is 22.7 and $3.5 \mu\text{s}$ in 6.0 M HCl–6.0 M LiCl solution and 0.1 M HCl solution, respectively (in 0.1 M HCl, emission decay appears to be biphasic).

NDC). The emission decay was followed by a Jobin–Yvon H20V spectrophotometer and a photomultiplier R-955 of Hamamatsu Photonics. The signal was analyzed by the use of a TS-8121 stragescope of Iwasaki Electric Co. and a microcomputer HP-86 of Hewlett Packard. The measurements under high pressure (up to 200 MPa) will be described in detail elsewhere [12].

Electronic absorption spectra were obtained by a JASCO UVIDEDEC-610 spectrophotometer.

Results

Preliminary Observations

The cluster ion, $[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]^{2-}$, showed very broad absorption maxima in the region from 310 to 350 nm. The absorption pattern in this region differs slightly in different solvents such as acetonitrile, methanol, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and aqueous hydrochloric acid of various concentrations. On irradiation by ultraviolet light at the region of the absorption maximum, broad red emission was observed centered at 765 nm*. The emission maximum and the half-width are the same regardless of the solvents. The emission intensity did not change on continuous irradiation at a given wavelength in acetonitrile and HCl solutions, but decreased with time in other solvents. The decrease in DMSO is so rapid that accurate emission intensity could not be determined. The rate of decrease is in the order, $\text{DMF} < \text{MeOH} < \text{DMSO}$. The decrease in the emission intensity was accompanied by an appreciable change in the absorption spectrum. The change in absorption spectra was not observed when the solutions were kept in the dark. Thus in these solvents the complex ion decomposes photochemically to a non-emitting species.

*The emission maximum in acetonitrile was reported to be at 760 [1] and 805 [2] nm.

Emission Lifetimes

Table 1 shows the emission lifetime (τ_{em}) and other characteristics of $[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]^{2-}$ in various solvents. Potassium or tetraethylammonium salt was used depending on the solubility in various solvents. In DMF which dissolves both salts, there was no difference in τ_{em} values when using K^+ ($82.2 \pm 0.7 \mu\text{s}$) or $(\text{C}_2\text{H}_5)_4\text{N}^+$ ($81.9 \pm 0.6 \mu\text{s}$) salts. The τ_{em} spans nearly two orders of magnitude from $3.7 \mu\text{s}$ in 0.6 M HCl to $180 \mu\text{s}$ in acetonitrile**. The values in acetonitrile [1, 2] and in 6 M HCl–6 M LiCl [2] are in good agreement with those reported previously (see footnote to Table 1).

It is seen that protic solvents tend to give smaller τ_{em} values. In HCl, however, smaller concentration gives smaller τ_{em} values. Since τ_{em} in 6 M HCl and in 6 M HCl–6 M LiCl are appreciably different, ionic strength or chloride ion concentration rather than proton concentration appears to be more influential. The τ_{em} value in acetonitrile is, on the contrary, insensitive to added electrolytes (see footnote to Table 1).

Pressure effect on τ_{em} was measured in the presence of dissolved dioxygen. Measurement under strictly air-free conditions is difficult with our pressure vessel [12]. Extrapolation of τ_{em} to $[\text{O}_2] = 0 \text{ M}$ from the measurements at various dioxygen concentrations indicated that τ_{em} at $[\text{O}_2] = 0 \text{ M}$ is independent of pressure in acetonitrile[†] and decreases significantly with increasing pressure in 0.6 M HCl (*c.* 40% decrease at 200 MPa from the value at ambient pressure).

**It is interesting that τ_{em} values under air saturated conditions fall within a narrow range from $7.2 \mu\text{s}$ (in methanol) to $13.1 \mu\text{s}$ (in DMF) including other solvents than those in Table 1 (e.g. ethanol, acetone and DMSO). The quenching by dioxygen ($k_{\text{q}}(\text{O}_2)$) effectively competes with the solvent dependent 'non-radiative decay' process (see text). The τ_{em} values in deoxygenated aqueous HCl are not significantly different from those in the same solvent under air-saturated conditions.

[†]Activation volume for the quenching reaction rate by dioxygen in acetonitrile was estimated to be *c.* $-8 \text{ cm}^3 \text{ mol}^{-1}$.

Emission Quantum Yields

Table 1 shows the emission quantum yields obtained by the procedure described in 'Experimental'. It is seen that ϕ_{em} decreases as τ_{em} decreases. When the relations (1) and (2) were applied to the present data, radiative rate constant (k_r) and 'non-radiative rate constant' (k_{nr}) were obtained as in Table 1.

$$\phi_{em} = k_r / (k_r + k_{nr}) \quad (1)$$

$$\tau_{em} = 1 / (k_r + k_{nr}) \quad (2)$$

The radiative decay (k_r) is almost constant in various solvents. The remarkable solvent effect on τ_{em} should be due to the difference in 'non-radiative' decay rate (k_{nr}), which spans nearly two-orders of magnitude.

Discussion

The ' k_{nr} ' should include all non-radiative decay processes such as non-radiative thermal decay (k_{na}) of the emissive state, the decay from different non-emissive states (k_{nb}), and the decay by chemical reactions (k_{nc}). The k_{nr} can then be expressed by (3).

$$k_{nr} = k_{na} + k_{nb} + k_{nc} \quad (3)$$

It has been pointed out that the emissive excited state and the ground state of $[(Mo_6X_8)X_6]^{2-}$ clusters ($X^- = Cl^-, Br^-$) are localized largely at the Mo_6 cluster unit on the basis of the insensitiveness of absorption and emission energies to the halide ions [2, 5]. Unusually large non-radiative lifetimes could be related to the isolated excited state at the inside of the complex ion, and the decay through the interaction with surrounding halide ligands is not favorable. It may be expected then that the photophysical properties of $[(Mo_6Cl_8)Cl_6]^{2-}$ would be insensitive to the solvational and ion-associational environments in solution. Similar τ_{em} values of $[(Mo_6Cl_8)Cl_6]^{2-}$ in acetonitrile (180 μs) and in the solid state (120 μs at 300 K [1]) would indicate that the emissive excited state and probably ground state energies of the Mo_6 unit are virtually unaffected by the solvation in acetonitrile. The insensitiveness of τ_{em} to the added electrolytes and pressure in acetonitrile support that the complex ion in this solvent is rather close to the isolated ion in the crystalline state. It is concluded that k_{nc} , the pathway involving photochemical reaction, is not important in acetonitrile.

Observed independence of the emission energies on the solvents suggests that the emissive excited state and the ground state levels are unaffected by the solvents. It follows that k_{na} must not be responsible for the difference in k_{nr} . In fact, for some systems in which environmental effect on k_{nr} is interpreted on the basis of the vibrational coupling mechanism (k_{na}), there is a good linear correlation between k_{nr} and the emission energy [13]. The k_{na} of the

present hexamer should be almost constant throughout the solvents examined, since the observed large change in k_{nr} is not accompanied by the shift in the emission energy.

Temperature dependence of the emission lifetime of the crystalline solid of $[(C_2H_5)_4N]_2[(Mo_6Cl_8)Cl_6]$ indicates the existence of splitting sub-levels within the energy gap of the Boltzmann distribution [6, 11]. All these levels should be insensitive to the solvents, as far as k_r , which represents the combination of all these emissive levels, is insensitive to the solvents.

For considering the solvent independent k_{nb} pathway, we must assume the participation of a non-emitting energy level slightly above the emissive level. The new energy state should interact with solvent molecules to change its energy so that the Boltzmann distribution changes with respect to the emissive state. If the postulated energy state was solvent sensitive, then it should be more sensitive to the difference in the coordinated halide ions. $[(Mo_6Cl_8)Cl_6]^{2-}$ and $[(Mo_6Br_8)Br_6]^{2-}$ show, however, very similar τ_{em} values to each other in acetonitrile as well as in the solid state. It is thus difficult to account for the observed difference in k_{nr} by a mechanism through the k_{nb} pathway.

The only remaining and the most plausible mechanism accounting for the observed large solvent effect on k_{nr} is the chemical reaction pathway (k_{nc}). It is proposed that photochemical cleavage of one or some Mo-Cl (terminal) bonds takes place from the emissive excited state. Observation of the photochemical decay of the hexanuclear ion on continuous irradiation in some solvents supports this decay mechanism. No decomposition was observed in HCl solutions which provides the most efficient 'non-radiative decay'. In HCl, products of the photochemical aquation could undergo rapid back reaction with co-existing chloride ions to preserve the original ion.

Significant influence by solvent indicates that the solvent molecules must participate in the photochemical dissociation of the Mo-Cl (terminal) bond. The trend in HCl in various concentrations is interpreted by considering that the ion-pair with potassium ions or hydronium ions is less active to the photochemical reaction. The ion-pairs are solvated to a lesser extent due to weaker electrostatic attraction, while solvents would assist the photochemical Mo-Cl bond fission. Importance of the solvent molecules in the photochemical bond cleavage is further supported by the high pressure studies in 0.6 M HCl. Since the pressure effect is not observed in acetonitrile, the observed pressure effect on τ_{em} in 0.6 M aqueous HCl should reflect the pressure dependence of k_{nc} . It is concluded that the photochemical Mo-Cl (terminal) bond cleavage occurs through associative attack by a solvent molecule on the basis of the observed negative activation volume [14]. If the k_{nr} value in acetonitrile is assumed to represent intrinsic k_{na} and k_{nb} processes

(k_{nc} is assumed to be negligible in acetonitrile), then the k_{nc} value in each solvent is calculated as in the last column of Table 1*.

From the theoretical consideration, the lowest excited state of $[(Mo_6Cl_8)Cl_6]^{2-}$ has predominantly d_z^2 character, and it is plausible that the occupation of the excited state would weaken the Mo–Cl bond [11].

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research (No. 62540455 and 63540470) to Y.S. from the Ministry of Education, Science and Culture of Japan, and also by the Joint Studies Program (1986–1987) of the Institute for Molecular Science. The authors thank Professor T. Azumi, Tohoku University, for his valuable discussions.

*From the linear relationship of $1/k_{nc}$ against I (I = ionic strength), the k_{nc} value in pure water is extrapolated to be $c. 5 \times 10^5 \text{ s}^{-1}$.

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