

Effect of Cations on the Phosphorescence Properties of Acetophenone Derivatives with a Crown Ether Moiety

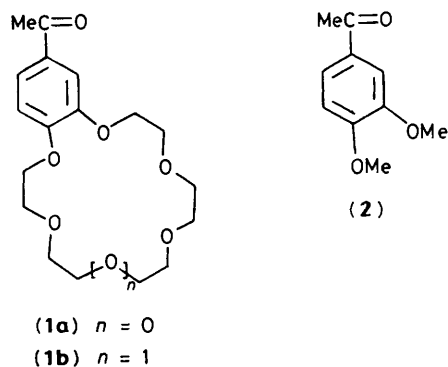
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The phosphorescence quantum yields (ϕ_p) of acetophenone derivatives bearing a crown ether moiety are markedly altered by complexation with alkali and alkaline earth metal cations.

The binding of alkali metal cations to crown ethers is a well-known phenomenon.¹ Although it is of interest to study the effect of cation binding on the photophysical properties of functionalized crown ethers, little attention had been given to the excited states of such complexes until recently.²⁻⁶ We report here the effect of cations on the lifetimes (τ_p) and quantum yields (ϕ_p) of phosphorescence of aromatic ketones with a crown ether moiety, 4'-acetobenzo-15-crown-5 (**1a**), 4'-acetobenzo-18-crown-6 (**1b**), and 3',4'-dimethoxyacetophenone (**2**).

The complexation of alkali and alkaline earth metal cations by (**1a**) and (**1b**) was confirmed by extraction of their picrate salts.¹ The complexation of cations by (**1a**) and (**1b**) was also ascertained by a slight shift to shorter wavelength of the absorption spectrum of (**1a**) and (**1b**) on addition of cations. No significant binding of cations to (**2**) was observed. Although no fluorescence of (**1a**), (**1b**), or (**2**) was observed under the present experimental conditions as reported for acetophenone,⁷ the same broad and structureless phosphorescence was observed in the 400–600 nm region. The



excitation was carried out using light of 330 nm wavelength. Table 1 lists ϕ_p and τ_p of **(1a)**, **(1b)**, and **(2)** in the presence of tenfold excesses of alkali and alkaline earth metal chlorides. ϕ_p and τ_p were measured in uncracked ethanol-methanol (4:1) glasses at 77 K.† All samples were thoroughly degassed by freeze-pump-thaw cycles on a high vacuum line. The ϕ_p values for **(1a)**, **(1b)**, and **(2)** without added salts were 0.26, 0.47, and 0.52, respectively. The ring tension caused by a crown ether moiety as a substituent of acetophenone seems to reduce the ϕ_p . Although τ_p of **(1a)**, **(1b)**, and **(2)** was almost unchanged on addition of cations, complexation of cations by **(1a)** and **(1b)** caused both increase and decrease in ϕ_p , depending on the kind of cations. ϕ_p for **(2)** slightly decreased on addition of all cations except CaCl_2 . However, a change in ϕ_p characteristic of cations added was not observed. An enhanced ϕ_p was observed for **(1a)**- Cs^+ , **(1b)**- Cs^+ , and **(1b)**- Rb^+ systems. Complexation of cations other than Cs^+ and Rb^+ by **(1a)** and **(1b)** caused a decrease in ϕ_p and a remarkable decrease in ϕ_p was observed for **(1a)**- Na^+ , **(1b)**- Ba^{2+} , **(1b)**- Sr^{2+} , and **(1b)**- Ca^{2+} systems. For alkaline earth metal cations, ϕ_p of **(1a)** and **(1b)** decreased in the order $\text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$, which was consistent with the order of the binding strength of cations by benzo-15-crown-5 and benzo-18-crown-6.⁸ Thus an introduction of a charge into the crown ether cavity by complexation seems to reduce ϕ_p .

† The excitation slit width was kept at 3 nm. ϕ_p was determined by comparison of the intensities of the phosphorescence spectra of **(1)**, **(1b)**, and **(2)** with that of *p*-methoxyacetophenone ($\phi = 0.68$)⁹ having the same optical density at the excitation wavelength. The phosphorescence decays of the samples were exponential.

Table 1. Phosphorescence quantum yields (ϕ_p) and lifetimes (τ_p) of **(1a)**, **(1b)**, and **(2)** in degassed ethanol-methanol (4:1) glasses at 77 K.^a

Salt added	(1a)		(1b)		(2)	
	τ_p/s	ϕ_p	τ_p/s	ϕ_p	τ_p/s	ϕ_p
None	1.1	0.26	1.2	0.47	1.2	0.52
NaCl	1.1	0.077	1.2	0.45	1.2	0.46
KCl	1.2	0.21	1.2	0.44	1.2	0.43
RbCl	1.1	0.19	1.1	0.55	1.2	0.42
CsCl	1.0	0.38	1.0	0.73	1.1	0.44
CaCl_2	1.1	0.24	1.1	0.16	1.2	0.53
SrCl_2	1.1	0.17	1.0	0.075	1.2	0.48
BaCl_2	1.1	0.16	1.0	0.057	1.1	0.48

^a Concentrations of acetophenone derivatives and salts added are $1.0 \times 10^{-4} \text{ mol l}^{-1}$ and $1.0 \times 10^{-3} \text{ mol l}^{-1}$, respectively. The wavelength of the excitation light is 330 nm.

without remarkable change in τ_p , if there is no heavy atom effect operating for Cs^+ and perhaps Rb^+ , which increases ϕ_p by increasing the rate constant for phosphorescence, as observed for 2,3-naphtho-20-crown-6.^{2,3} A blue shift in phosphorescence was observed for the **(1a)**- Na^+ (6 nm), **(1b)**- Ba^{2+} (13 nm), and **(1b)**- Sr^{2+} (8 nm) systems, suggesting a change in energy level of the excited triplet state on complexation.

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