*Inorganica Chimica Acta*, *117* (1986) 87–89

# Absorption and Emission Properties of Divalent Ytterbium Crown Ether Complexes

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(Received January 8, 1986)

## Abstract

New complexes between $YbCl_2$ and crown ethers have been studied. Luminescence of the complexes are observed for the first time. Enhancement of the emission intensity and a shift of the emission peak are a result of the formation of the complexes. Absorption spectra correspond with the transition of a $Yb^{2+}$ ion between $4f^{14}$–$5d4f^{13}$.

## Introduction

Luminescence properties of a $Yb^{2+}$ ion in an inorganic solid host, for example, silica glass, alkali halides and alkali earth halides have been reported in detail [1–6].

Adachi *et al.* [7, 8] and Donohue [9] have studied the fluorescence given by methanol solutions of crown complexes with $Eu^{2+}$. Sabbatini *et al.* [10, 11] have described absorption and emission properties of $Eu^{2+}$ cryptates in aqueous solution.

A divalent ytterbium ion is also stable in solution but to a lesser extent. Formation of a crown complex with $Yb^{2+}$ increases the stability of its divalent state. Luminescence of $Yb^{2+}$ crown complexes has not been reported yet. This paper describes the fluorescence properties of the $Yb^{2+}$ complexes formed by the reaction between anhydrous $YbCl_2$ and crown ethers.

## Experimental

Solutions of divalent ytterbium polyether complexes used in this study were obtained by dissolving anhydrous $YbCl_2$ and polyethers in anhydrous degassed methanol. The polyethers used as ligands are illustrated in Fig. 1.

$YbCl_2$ was prepared from $Yb_2O_3$ (99.99%) which was mixed with an excess of $NH_4Cl$ and then fired at 700 °C for 3–4 h, at 850 °C for 0.5 h and decreased slowly to room temperature in a hydrogen atmosphere. A deep green powder of $YbCl_2$ was obtained. Absorption spectra were observed using a Shimadzu double beam spectrophotometer, model UV 180. Emission and excitation spectra were determined on a Shimadzu absolute spectrofluorophotometer, model RF-502, equipped with an automatic compensation and procalibration system. Fluorescence quantum yields were determined by comparing the intensity of samples with that of a solution of $1 \times 10^{-5}$ M quinine bisulfite–0.1 N $H_2SO_4$ ($\phi = 0.55$) [12]. The excitation wavelength for the standard quinine solution was 365 nm.

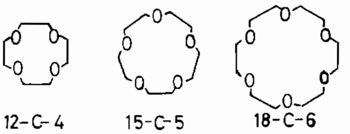

Fig. 1. Schematic representation of ligand used in this paper.

## Results and Discussion

### *The Spectroscopic Properties of $Yb^{2+}$–18-C-6*

The typical absorption and emission spectra of a methanolic solution of $Yb^{2+}$–18-C-6 complexes as well as those of $YbCl_2$ are given in Fig. 2. For the purpose of comparison, Fig. 3 also shows the absorption spectra for the complexes of $Yb^{2+}$–12-C-4 and $Yb^{2+}$–15-C-5 in methanol and $YbCl_2$ in $H_2O$.

The emission spectra are composed of broad bands due to the transition between the $5d4f^{13}$

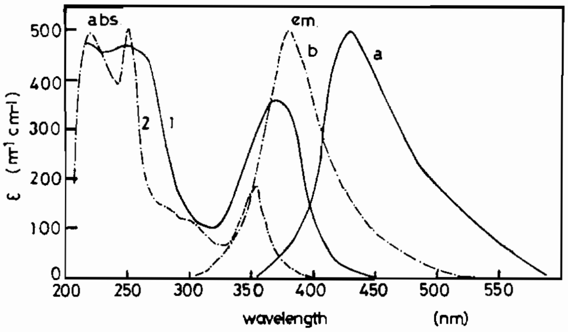

Fig. 2. Absorption and emission spectra of $Yb^{2+}$–18-C-6 complex and $YbCl_2$ in methanol. (1) Absorption spectrum of a, emission spectrum of $YbCl_2$ in methanol; (2) absorption spectrum of b, emission spectrum of $Yb^{2+}$–18-C-6 complex.

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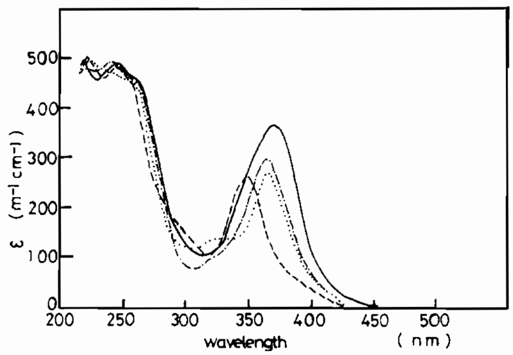

Fig. 3. Absorption spectra for $Yb^{2+}$–12-C-4, $Yb^{2+}$–15-C-5 in methanol and $YbCl_2$ in $H_2O$ or in methanol. $YbCl_2$ in methanol, ——; $Yb^{2+}$–12-C-4, – · –; $Yb^{2+}$–15-C-5, · · ·; $YbCl_2$ in $H_2O$, - - -.

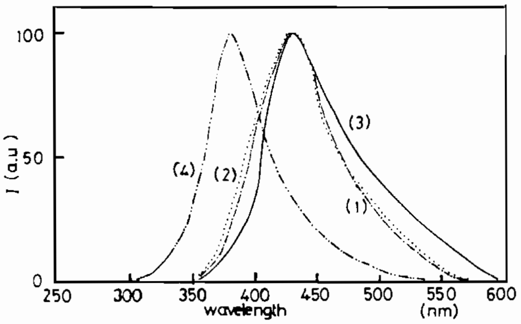

Fig. 4. Emission spectra of $Yb^{2+}$–12-C-4 and $Yb^{2+}$–15-C-5 complexes in methanol. (1) $Yb^{2+}$–12-C4, (2) $Yb^{2+}$–15-C-5, (3) $YbCl_2$, (4) $Yb^{2+}$–18-C-6.

and $4f^{14}(^1s)$ states. Assignment of the absorption spectra will be discussed in detail in the last section.

When the complexes between $Yb^{2+}$ and 18-C-6 are formed, some shift of absorption and emission bands to a shorter wavelength, the fine structure of absorption bands (see curve 2 in Fig. 2) and the narrowing of the half-width of the absorption bands can be observed. The splitting and decrease of the band widths of the absorption bands are also seen. These phenomena might be caused by the lower symmetry of the organic ligand environment. A noticeable difference in the spectroscopic characteristics between $Yb^{2+}$–18-C-6, and $Yb^{2+}$–12-C-4 or $Yb^{2+}$–15-C-5, as shown in Figs. 3 and 4, is due to the larger cavity size of 18-C-6 ring (1.4 Å) than that of 12-C-4 (0.6 Å) or 15-C-5 (0.9 Å) rings. In other words, 12-C-4 and 15-C-5 have difficulty in forming complexes with $Yb^{2+}$ (radius 1.06 Å) because of their small cavity size.

In absorption spectra of $YbCl_2$ in water three heavy diffuse maxima are observed in the UV region, as shown in Fig. 3, somewhat inconsistent with the result of Butement [13]. The shape of the spectrum is different from that of $YbCl_2$ in methanol. There are shifts of the bands to a shorter wavelength and a narrowing of the bands, due to the difference in polarity effect between water and methanol.

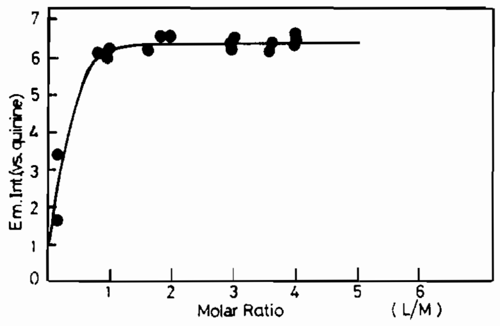

Fig. 5. Molar ratio [L/M] plots of emission intensity for $Yb^{2+}$–18-C-6 complex.

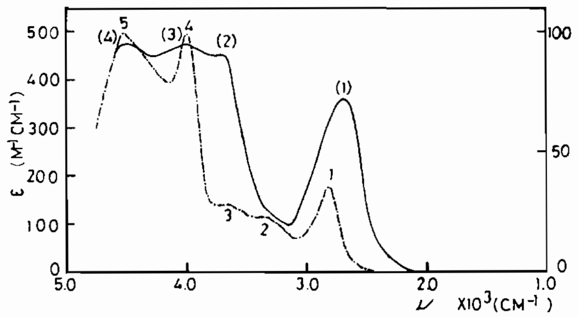

Fig. 6. Absorption spectra for $Yb^{2+}$–18-C-6 (· · ·) and $YbCl_2$ (——) in methanol. Abscissa is indicated by wavenumbers.

### Stoichiometry and Fluorescence Intensities of the Complexes

A gradual addition of 18-C-6 into a methanol solution of $YbCl_2$ resulted in a shift of the absorption bands towards a higher energy as shown in Fig. 4, and an increase in emission intensity which reached a maximum after approximately 1 equivalent of the ligand had been added to $Yb^{2+}$ (see Fig. 5). The stoichiometry of the 1:1 (Yb:ligand) is the same as that of the complex of $Eu^{2+}$ with 18-C-6 [14].

Luminescence quantum yields observed from absorption and emission intensity are about 0.03% for the methanol solution of $YbCl_2$ and 1% for the complex of $Yb^{2+}$–18-C-6. The enhancement of the luminescence by a factor of about 20–30 seems to be due to the limiting interaction of ions in the 18-C-6 complex with solvent molecules [7, 8]. As described above, 12-C-4 or 15-C-5 does not increase the emission intensity at all.

### Assignment of Electronic Transition

Assignment of the luminescence transition of $Yb^{2+}$ corresponds to the $4f^{14}$–$5d4f^{13}$ configuration [15, 16]. When $Yb^{2+}$ is in the ligand field the situation of

TABLE I. $4f^{14}$–$4f^{13}5d$ Absorption Peaks and their Assignment for $YbCl_2$ in Methanol and $Yb^{2+}$–18-C-6 Complex

| Compounds | Peak number[a] | Absorption peaks | | Corresponding levels |
|---|---|---|---|---|
| | | ($\times 10^3$ cm$^{-1}$) | (nm) | |
| $Yb^{2+}$–18-C-6 | 1 | 28.0 | 355 | $5d(e_g)4f^{13}(^2F_{7/2})$ |
| | 2 | 33.0 | 303 | $5d(e_g)4f^{13}(^2F_{7/2})$ |
| | 3 | 37.0 | 270 | $5d(t_{2g})4f^{13}(^2F_{5/2})$ |
| | 4 | 40.0 | 250 | $5d(t_{2g})4f^{13}(^2F_{5/2})$ |
| | 5 | 45.0 | 220 | $5d(t_{2g})4f^{13}(^2F_{5/2})$ |
| $YbCl_2$ in methanol | (1) | 27.0 | 370 | $5d(e_g)4f^{13}(^2F_{7/2})$ |
| | (2) | 38.5 | 260 | $5d(t_{2g})4f^{13}(^2F_{5/2})$ |
| | (3) | 40.0 | 250 | $5d(t_{2g})4f^{13}(^2F_{5/2})$ |
| | (4) | 45.5 | 220 | $5d(t_{2g})4f^{13}(^2F_{5/2})$ |

[a] The numbers are those illustrated in Fig. 6.

the $5d4f^{13}$ configuration depends on the intensity of the coordination field [17].

Figure 6 shows the absorption spectra for $YbCl_2$ in methanol and the $Yb^{2+}$–18-C-6 complex. The absorption peaks shown in Fig. 6 and their assignments are given in Table I. The results are very similar to that of $Yb^{2+}$ in $SrCl_2$ host with a fluorite structure (space group, $O_h$) [18]. Therefore the absorption spectra of $Yb^{2+}$–18-C-6 in methanol would also consist of $e_g$ and $t_{2g}$ components of the 5d configuration with a separation of $10.7 \times 10^3$ cm$^{-1}$ [18]. Each of those 5d orbitals has a high partner, which corresponds to the $^2F_{5/2}$–$^2F_{7/2}$ transition of $Yb^{3+}$($4f^{13}$) at $10.0 \times 10^3$ cm$^{-1}$ (see Table I).

We can conclude that the absorption bands of $YbCl_2$ in methanol and of the $Yb^{2+}$–18-C-6 complex are attributed to two transitions,

$$4f^{14}–5d(e_g)4f^{13} \quad \text{and} \quad 4f^{14}–5d(t_{2g})4f^{13}.$$

## Acknowledgements

The authors wish to thank T. Mishima and H. Nakamura for their help in preparing samples.

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