A study on the fluorescence behaviour and structure of thulium's ion association compound Tm(BPMPHD)₂·CTMAB

Jinghe Yang*, Nianqin Jie, Guiling Zhang & Changlun Tong
Department of Chemistry, Shandong University, Jinan 250100, China
and
Hongmei Ge
The Import and Export Commodity Inspection Bureau of China Zibo 255310

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The fluorescence behaviour of the Tm-BPMPHD-CTMAB system and the affecting factors have been studied. The solid complex of Tm-BPMPHD has been synthesized. Tests indicate that the composition ratios are 1:2:1 for Tm:BPMPHD:CTMAB. From the IR and NMR spectra, it is found that in the Tm(BPMPHD)₂ complex, Tm³⁺ coordinates with four oxygen atoms of BPMPHD in its enol form. The structure of the Tm(BPMPHD)₂·CTMAB has been proposed. The luminescence mechanism is also discussed.

The compounds of thulium can be used as luminous materials and laser materials. Therefore it is important to study the luminous behaviour of any new thulium compound synthesised. Hardly any complex of Tm³⁺ in water solution can emit fluorescence of Tm³⁺, and no multicomplex fluorescence system of Tm³⁺ has been reported. We found that the artificial synthetic ligand, 1, 6-bi(1'-phenyl-3'-methyl-5'-pyrazolone-4'-carboxylato)hexanedione (BPMPHD), was a new fluorescence chelating agent of rare earth elements, which could form a ternary ion association compound with Tm³⁺ and cation surfactant, cetyltrimethylammonium bromide (CTMAB). Experiments showed that the ion association compound can emit strong intrinsic fluorescence of Tm³⁺ in water solution and the fluorescence intensity is enhanced nearly one time by adding a large amount of Gd³⁺ into the system.

The analytical application of Tm-BPMPHD-CTMAB system has been reported. In the present paper, the fluorescence behaviour and luminescence mechanism of Tm-BPMPHD-CTMAB system were reported along with the synthesis of solid Tm³⁺ complex and the determination of its composition and structure.

Notes

Experimental

All fluorescence intensities were measured on a 850-fluorescence spectrophotometer (Hitachi, Japan). All absorption spectra were measured on a UV-240 spectrophotometer (Shimadzu, Japan). All the reagents were of analytical reagent grade and distilled, deionized water was used throughout. Stock standard solutions (1.00 × 10⁻² mol dm⁻³) of reagent ions were prepared by dissolving the corresponding oxides (99.9%) in hydrochloric acid and diluting with distilled water. BPMPHD solution (1.0 × 10⁻³ mol dm⁻³) was prepared by adding the appropriate amount of BPMPHD into 95% (v/v) ethanol solution, and adding 1:1 NH₃·H₂O dropwise until BPMPHD dissolved completely. Aqueous CTMAB solution (1.0 × 10⁻² mol dm⁻³) was used. Hexamethylenetetramine (HMTA) solution (10%, w/w) was used as a buffer, the pH being adjusted to 5.5 with HCl.

Procedure

To a 25 ml test tube, standard solutions of reagent ions, CTMAB, BPMPHD and buffer solution were added in that order. The mixture was diluted to 10 ml with distilled water, shaken and allowed to stand for 20 min. The fluorescence intensity of Tm³⁺ was measured in a 1 cm quartz cell with excitation and emission wavelengths of 300 nm and 478 nm, respectively.

Synthesis of the solid complex of Tm³⁺

The solid complex of Tm-BPMPHD was synthesized according to the following procedure: Appropriate amount (about 1 mmol) of BPMPHD was weighed, put into 25 ml of 95% (v/v) ethanol and 1:1 NH₃·H₂O was added dropwise until the suspended solid of BPMPHD dissolved completely. Thulium oxide 0.25 mmol was weighed and dissolved in HCl solution; these two solutions were mixed and stirred for 30 min. in 80°C water bath. The precipitate was filtered off and washed several times with acidified water (pH = 2). After drying the precipitate, the unreacted ligand was eliminated by extractive crystallization with CHCl₃, and the crystal was vacuum dried until its weight remained constant.

Results and discussion

Absorption and fluorescence spectra

The absorption spectra of a series of Tm-BPMPHD systems, in which the concentrations of Tm³⁺ vary from 0
to $5.0 \times 10^{-6}$ mol dm$^{-3}$, are shown in Fig. 1. With the increase in Tm$^{3+}$ concentration in the system, the absorption peak (260 nm) of BPMPHD decreases constantly; at the same time, a new absorption peak occurs at 268 nm and its intensity increases continuously. All the curves passed one point which is called isoabsorptive point. It can be concluded that in the Tm-BPMPHD system a new compound was formed.

The fluorescence spectra of BPMPHD(1), Tm-BPMPHD(2) and Tm-BPMPHD-CTMAB(3) systems are shown in Fig. 2. From Fig. 2, it can be seen that the excitation spectra of the three systems are similar in shape and in the peak position (300 nm), which indicates that the fluorescence of the three systems is due to the energy absorbed by the BPMPHD. In systems (2) and (3), besides the emission of BPMPHD (350-550 nm), another emission peak is observed at 478 nm corresponding to the transition of Tm$^{3+}$ from $^1D_2$ level to $^3H_5$ level. In system (2), when Tm$^{3+}$ was added to the BPMPHD solution, the fluorescence intensity increased slightly. The reason is that Tm$^{3+}$ can complex with BPMPHD and form a compound with four quininy rings, the rigid plane structure of BPMPHD is strengthened and the absorption cross-section of BPMPHD is enlarged. Adding CTMAB to system (2), the fluorescence intensity can be enhanced 25 times. In addition, the fluorescence intensity of the Tm-BPMPHD-CTMAB system can remain stable at least for 24 h.

The composition and structure of the complex

From Figs 1 and 2, it can be seen that a complex is formed in Tm-BPMPHD-CTMAB system. Its composition was examined using the molar ratio method and the continuous variation method. The composition ratios were 1:2:1 for Tm:BPMPHD:CTMAB. So we assume that an ion association

**Reaction conditions of Tm$^{3+}$ with BPMPHD and CTMAB**

The effects of pH and buffer on the fluorescence intensity of the Tm-BPMPHD-CTMAB system are examined. Tests showed that the maximum intensity occurs in the range of pH 5.0-6.2 and 1.0 ml of HMTA-HCl solution (pH = 5.5) is the most suitable buffer.

Different kinds of surfactants have different effects on the fluorescence intensity of the system. Experiments indicated that the non-ionic and some cationic surfactants had enhancement effect, among which CTMAB is the best sensitizer. In comparison with the system without CTMAB, the fluorescence intensity of the system with CTMAB in the concentration range $1.0 \times 10^{-3}$-2.0 x $10^{-3}$ mol dm$^{-3}$ could be enhanced 25 times.

In addition, the fluorescence intensity of the Tm-BPMPHD-CTMAB system can remain stable at least for 24 h.
complex \([\text{Tm(BPMPHD)}_2]^{-}\text{CTMAB}^+\) was formed in the system.

After dissolving in 1:1 \(\text{HNO}_3\)-\(\text{HClO}_4\), the composition of the complex \(\text{Tm-BPMPHD}\) was determined by EDTA complexometric titration using xylene orange as an indicator. Experiments showed that there was one \(\text{Tm}^{3+}\) in one complex molecule.

The mass spectrum of the complex is shown in Fig.3. From Fig.3 it can be seen that the molecular ion peak and the molecular fragment peaks appear at 1083, 931, 855, 779 and 542, etc. These data prove that the molecular formula of the complex is \([\text{Tm(BPMPHD)}_2]\).

BPMPHD has two isomers (ketone and enol) in water solution, which is as follows:

In order to deduce with which atoms and in which form BPMPHD coordinated with \(\text{Tm}^{3+}\), we measured the IR spectra of the ligand and the complex. In the spectrum of the ligand, there are two strong peaks at 1630 cm\(^{-1}\) and 1559 cm\(^{-1}\), corresponding to the carbonyl vibration of 1-O, 4-O and 2-O, 3-O of BPMPHD, respectively. While in that of the complex the two peaks shift to lower wave number, 1616 cm\(^{-1}\) and 1494 cm\(^{-1}\), respectively. The shifts indicate that the coordinative atoms are the four oxygen atoms. Furthermore, because the shift of the vibration peak of 2-O, 3-O is greater than that of 1-O, 4-O, it can be concluded that in the complex \(\text{Tm}^{3+}\) coordinated with BPMPHD in its enol form.

The nuclear magnetic resonance (NMR) spectra of both the ligand and the complex are shown in Fig.4. It can be seen that the proton peak of enol form of BPMPHD at 10.8 ppm disappears in the NMR spectrum of the complex, which indicates that it is enol form that BPMPHD coordinates with \(\text{Tm}^{3+}\).

Based on the above results, we propose that the structure of the ternary ion association compound is as shown in I.

**Luminescence mechanism**

Tests showed that an ion association compound \([\text{Tm(BPMPHD)}_2]^{-}\text{CTMAB}^+\) was formed and dissolved in CTMAB micelles in the \(\text{Tm-BPMPHD-CTMAB}\) system. From the excitation spectra (Figs 1 and 2), it can be seen that the absorption of
[Tm(BPMPHD)₂⁻ CTMAB⁺ in the neighbourhood of 300 nm is due to that of BPMPHD in the complex. We think that the system emits intrinsic fluorescence of Tm³⁺ due to the intramolecular energy transfer. After absorbing light energy, the excited BPMPHD is not stable, it soon undergoes a radiationless transition to its triplet state. The energy of the BPMPHD triplet can be transferred to the ¹D₂ level of Tm³⁺. Corresponding to the transition from ¹D₂ to ³H₅, the complex emits the intrinsic fluorescence of Tm³⁺. This luminescence of the complex belongs to M*-M luminescence mechanism.

The essential condition of M*-M complex luminescence is that the triplet level of the ligand must be higher than the luminescence level of metal ion. Test showed that the Tm-BPMPHD system emitted the fluorescence of Tm³⁺ while no fluorescence of Gd³⁺ was observed. Hence, we concluded that the triplet level of BPMPHD is between the ⁹P₇/₂ level of Gd³⁺ (32066 cm⁻¹) and the ¹D₂ level of Tm³⁺ (27900 cm⁻¹).

CTMAB could greatly enhance the fluorescence intensity of the system by a factor of 20%. (2) CTMAB micelles dissolved the ion association complex in them and avoided the collision between the complex molecules and the water molecules, thus decreasing the radiationless energy loss and increasing the fluorescence quantum yield of the system greatly.

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References
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