Notes

Synthesis and characterization of cryptates of Sm(III), Eu(III), Tb(III), Dy(III) chlorides with macrobicyclic cryptand

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Four novel solid cryptates of a cage-type diazahexaoxa hexabarbitone-cryptand (L) with RE(III) (RE=Sm,Eu,Tb,Dy) chlorides have been synthesized and characterized by IR, fluorescence spectra, TG-DTA and molar conductances. The composition of these cryptates is found to be RE₂CI₆L·nH₂O and the intensity at 490 nm (ε₄₉₀ ≈ 7 F₆) is five times that at 547 nm (ε₅₄₇ ≈ 7 F₅) in cryptate.

Rare earth cryptates with macrocyclic cryptands are important because they display several unusual characteristics, such as high thermodynamic stability, kinetic inertness in water and stabilization of the +2 oxidation state of the lanthanide elements by means of forming cryptates and as new luminescent materials and potential labels for luminescence immunoassays. Therefore, as an extension of our previous studies on the synthesis, characterization, and fluorescent properties of rare earth cryptates, the present paper reports the synthesis and characterization and fluorescence of the cryptates of Sm(III), Eu(III), Tb(III) and Dy(III) chlorides with a rigid cryptand L.

Experimental

The rare earth oxides (RE₂O₃, except for Tb₂O₅) were obtained from Shanghai Yue Long Chemical Factory and were at least of 99.99% purity. Rare earth(III) chlorides were prepared by the reaction of rare earth oxides with 1:1 hydrochloric acid. All other materials were at least of reagent grade and were purified or dried by standard methods.

The contents of the rare earth ions in the lanthanide cryptates were determined by EDTA titration. Carbon, hydrogen, and nitrogen analyses were performed on an Elementar Vario EL elemental analyser. IR spectra in the region 4000-250 cm⁻¹ were recorded with a Nicolet Model FT-170 SX IR spectrophotometer using KBr pellets. Conductance measurements were carried out in 10⁻³ mol dm⁻³ dimethylformamide solution at 25 °C using a Shanghai No.2 Instrument Factory DDS-11A conductometer. The cell constant was 0.92. Fluorescence spectra were obtained on a Hitachi-850 fluorescence spectro-photometer. TG-DTA data were obtained with PCT-2 precision thermobalance analyzer made in Beijing Optical Instrument Factory under air atmosphere at a heating rate of 5°C min⁻¹.

Preparation of the cryptand

The macrocyclic cryptand L was synthesized by the method of Atkinson. It was confirmed by IR,¹H-NMR and elemental analysis. Where L is a shorthand notation for 9, 12, 28, 31, 46, 49-hexaoxa-1, 20-diazahexabarbitone-cryptand-[18,18,18,0₃,₈,₁₃,₁₈,₂₂,₂₇,₃₂,₃₇,₄₀,₄₅,₅₀,₅₅]-hexapentaconta-3, 5, 7, 13, 15, 17, 22, 24, 26, 32, 34, 36, 40, 42, 44, 50, 52, 54-octadecene, schematically shown in Structure I.

Preparation of the cryptates

RE(III) chloride (0.20 mmol) in 15 ml of anhydrous acetonitrile was added to a stirred solution of the cryptand L (0.1 mmol) in 15 ml of hot anhydrous CHCl₃ and 2 ml of triethyl orthoformate under dry argon. After a few minutes, the RE(III) cryptate slowly formed as a microcrystalline product, and was refluxed for 6 h. The precipitates were...
filtered off, washed with acetonitrile, hot CHCl₃ and diethyl ether, respectively, and dried to constant weight in vacuo at room temperature.

Results and discussion

The elemental analysis results of the RE(III) cryptates are listed in Table 1. Their compositions correspond to the general formulae for RE₂Cl₆·nH₂O (RE = Sm, Tb, Dy, n=4; RE = Eu, n=5). All the cryptates are white microcrystalline and soluble in DMF and DMSO, insoluble in water and the other organic solvents. The molar conductances at 25°C of 10⁻⁵ mol/L solutions of the cryptates have been determined in DMF (λₑₑₑ = 52.1–56.7 S cm² mol⁻¹). All the chloride cryptates are non-electrolytes.

IR spectra

The cryptates have similar IR spectra which indicates that they have similar structures. The free cryptand exhibits Ar-O·CH₂ stretching band at 1240 cm⁻¹ that is shifted to lower frequencies by ca. 32 cm⁻¹ upon cryptation. This lowering of energy results from the metal-ether oxygen interaction upon cryptation. The νOH band appears in all cryptates as a broad absorption at ca. 3350 cm⁻¹. Additionally, they also show bands at ca. 536-548 cm⁻¹ assigned to rocking or wagging modes of coordinated water. The presence of water existing in two different ways is supported by the results of thermogravimetric analysis. In the region of 400-200 cm⁻¹, we expect to observe metal-ligand and metal-anion stretching frequencies. Two new bands were observed in the regions of 361-372 and 278-285 cm⁻¹ in the spectra of these cryptates, which are not present in those of the free ligand. These bands may be assigned to RE-O(ligand) and RE-N(ligand) stretchings, respectively. The νRE-Cl absorption bands in the regions of 240-247 and 255-266 cm⁻¹ were also observed which indicates the existence of coordinated chloride ions. This remains to be confirmed by X-ray single-crystal structure analysis.

TG-DTA analyses

TG-DTA analyses in all the cryptates show that they exhibit similar thermal analysis diagrams. They have two endothermic peaks on the DTA curve and have two obvious weight-losses on the TG curve. The Sm(III) cryptate loses two lattice water molecules and two coordinate water molecules when heated to 74°C and 142°C respectively. The mass loss are 2.9 and 2.6% respectively (calcd. 2.7 and 2.7%, respectively). The TG-DTA curve of the Sm(III) cryptate are similar to those of the other cryptates (for Eu cryptate, three lattice water molecules). The second endothermic peak corresponds to much higher temperature than 100°C which indicates the existence of the coordinated water and is in agreement with IR spectra.

All the cryptates have no melting point. The dehydrated cryptates are stable up to at least 250°C. Three or four, mainly exothermic, peaks appear successively on the DTA curve and obvious weight-loss can be seen from the TG curve. It can be seen that the cryptates are thermally less stable because they have lower initial decomposing temperatures. In addition, the final product was RE₂O₃ (for Tb cryptate, Tb₂O₇) when the temperature was above 850°C, and the total weight loss of the cryptates was found to be nearly equal to the calculated values.

Fluorescence spectra

When solid cryptates were irradiated with UV light (λ = 254 nm), the Eu₂Cl₆·5H₂O and Tb₂Cl₆·4H₂O exhibited red and green fluorescence, respectively. The Sm and Dy cryptates exhibits very weak fluorescence. The fluorescence spectra for RE(III) (RE = Eu, Tb) cryptates in the solid state and their assignments are given in Table 2. It can be seen that the emission intensity of these cryptates is not strong upon cryptate formation, which indicates that the intramolecular energy transfer to the metal ion in the cryptates is not an efficient process. It is probable that the introduction of six aromatic rings into macrobicyclic cryptand influences the energy of cryptand triplet states in the cryptates so that it is well unmatched with that of the metal emitting state in the cryptates. In addition, it should be noted that the fluorescence intensity of the Tb cryptate is the

<table>
<thead>
<tr>
<th>Cryptate</th>
<th>Yield (%)</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>RE</th>
<th>λₑₑₑ (S cm² mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm₂Cl₆·4H₂O</td>
<td>65.3</td>
<td>43.47(43.20)</td>
<td>4.11(4.20)</td>
<td>1.98(2.10)</td>
<td>22.40(22.55)</td>
<td>54.4</td>
</tr>
<tr>
<td>Eu₂Cl₆·5H₂O</td>
<td>68.2</td>
<td>42.56(42.52)</td>
<td>4.44(4.28)</td>
<td>2.05(2.07)</td>
<td>22.82(22.44)</td>
<td>57.6</td>
</tr>
<tr>
<td>Tb₂Cl₆·4H₂O</td>
<td>57.8</td>
<td>42.57(42.65)</td>
<td>4.31(4.15)</td>
<td>2.14(2.07)</td>
<td>23.73(23.53)</td>
<td>57.8</td>
</tr>
<tr>
<td>Dy₂Cl₆·4H₂O</td>
<td>45.0</td>
<td>42.12(42.42)</td>
<td>4.19(4.12)</td>
<td>2.08(2.06)</td>
<td>23.41(23.94)</td>
<td>52.1</td>
</tr>
</tbody>
</table>
Table 2 — The fluorescent data for the cryptates in the solid state

<table>
<thead>
<tr>
<th>RE</th>
<th>$\lambda_{Ex}$ (nm)</th>
<th>$\lambda_{Em}$ (nm)</th>
<th>Emission intensity [I.a.u.]</th>
<th>Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu</td>
<td>365</td>
<td>591</td>
<td>0.032</td>
<td>$^5D_0 \rightarrow ^7F_1$</td>
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<tr>
<td></td>
<td></td>
<td>612</td>
<td>0.092</td>
<td>$^5D_0 \rightarrow ^7F_2$</td>
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<tr>
<td></td>
<td></td>
<td>699</td>
<td>0.021</td>
<td>$^5D_0 \rightarrow ^7F_{4,5}$</td>
</tr>
<tr>
<td>Tb</td>
<td>340</td>
<td>490</td>
<td>0.473</td>
<td>$^5D_0 \rightarrow ^7F_{4,5}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>547</td>
<td>0.101</td>
<td>$^5D_0 \rightarrow ^7F_{5}$</td>
</tr>
</tbody>
</table>

* $\lambda_{Ex}$ = excitation wavelength, $\lambda_{Em}$ = emission wavelength, I.a.u. = relative intensity with arbitrary unit.

strongest among all the cryptates. Moreover, the intensity at 490 nm is found to be five times as that at 547 nm, which is seldom found in Tb complexes reported. This result may be in relation to the structure symmetry of the cryptates.

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References