

EXAFS study for the formation of glassy states of acylaminocarboxylato-yttrium and europium(III) complexes

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Introduction

We have been studying the preparations and the formation of glassy states for the acylaminocarboxylato metal (such as lanthanides and calcium) complexes. These systems are utilized to correlate the molecular structures with the ordering of the molecular assemblies in solids and in solutions [1, 2]. In this study, we have prepared the yttrium and europium complexes and measured the EXAFS for their concentrated solutions, glassy states, and crystalline states. We have focused on the change in the coordination numbers around the lanthanide ion depending on the states of the molecular assemblies.

Experimental

The metal complexes of acylaminocarboxylates were prepared by the reactions of lanthanide chlorides with potassium acylaminocarboxylate (1:3 molar ratios) in methanol. After the evaporation of the solvent, the residual solid was dissolved in ethylacetate. From the ethylacetate solution the glassy solid was isolated by an addition of acetone while the crystalline solid was isolated by an addition of water. For a comparison, lanthanide octanoates were prepared by the reaction between sodium octanoates and lanthanide nitrate according to a literature.

EXAFS measurements were performed at room temperature in a transmission mode at BL-7C and BL-9C. The solid samples were mixed with boron nitride to make a tablet specimen. The solution samples were sealed into polyethylene bags for measurements, and the metal concentration of [La] in these solutions is in the range of 0.1-0.8 (mol/L). In order to extract the backscattering amplitude and phase shift functions for the curve-fitting, the reference compounds (Y₂O₃ and Eu₂O₃ solids) were used in this experiment. The structural parameters were determined referred to those for these oxides.

Results and Discussion

Table 1 shows the coordination numbers (C.N.) and bond distances (*r*) of the concentrated solutions of yttrium and europium complexes. In the Fourier transforms of all the samples (not shown in this report), the peak around 0.23 nm assigned to the bond of Y-O appears with the same height.

Table 1. Structural parameters from EXAFS analysis of the acylaminocarboxylato-yttrium and europium complexes.

Sample	Bond	C.N.	<i>r</i> /nm
Y(octnt) ₃ H ₂ O powder	Y-O	7.7	0.235
Y(oct-ala) ₃ H ₂ O glass	Y-O	7.5	0.232
Y(oct-ala) ₃ 0.5H ₂ O glass	Y-O	8.1	0.232
Eu(hex-ala) ₃ H ₂ O glass	Eu-O	8.0	0.242
Eu(oct-ala) ₃ H ₂ O glass	Eu-O	8.0	0.244
Eu(oct-ala) ₃ 2H ₂ O crystal	Eu-O	8.0	0.243
Eu(dec-ala) ₃ H ₂ O glass	Eu-O	7.4	0.242
Eu(dod-ala) ₃ H ₂ O glass	Eu-O	6.8	0.246
Eu(oct-ala) ₃ 0.5M methanol soln	Eu-O	8.2	0.243
Eu(oct-ala) ₃ 1.0M methanol soln	Eu-O	8.0	0.244
Eu(oct-ala) ₃ 1.5M methanol soln	Eu-O	7.8	0.243

In a comparison among the octanolyalaninates and octanoate yttrium complexes, both the bond lengths and the coordination numbers are almost independent on the states. The number of hydration water is deficient in Y(octnt)₃H₂O from the viewpoint of the oxygen coordination numbers around the lanthanide metal. It is possible that the water coordinates to yttrium by bridging between the two metal atoms in the solid states. In the acylalaninate complexes, two carbonyl oxygens in the alaninate headgroup may coordinate to the lanthanide metals to make the coordination number eight. It is characteristic that the coordination number is reduced with an increase in the carbon numbers from C8 (oct-ala) to C12 (dod-ala). This result means that the longer the alkyl chains the weaker the coordination of the ligands. The detailed analysis is in progress.

References

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