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Use of the macrocyclic ligand cucurbit[6]uril for isolation of tetranuclear lanthanide aquahydroxo-carboxylate complexes from aqueous solutions

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Abstract

The tetranuclear lanthanide complexes $\{[\text{Ln}_4(\mu_3\text{-OH})_4(\mu_2\text{-OH})_2(\text{C}_5\text{NH}_4\text{COO})_2(\text{H}_2\text{O})_4\text{-}(\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12})_2][\text{Ln}(\text{H}_2\text{O})_8]1.5[\text{Ln}(\text{H}_2\text{O})_6(\text{NO}_3)_2]0.5\}(\text{NO}_3)_9 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Ho}, \text{Gd}, \text{or Er}$) were prepared by heating (130 °C) aqueous solutions of lanthanide nitrates, cucurbit[6]uril ($\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12}$), and 4-cyanopyridine. The tetradentate coordination of the macrocyclic cucurbit[6]uril ligands through the portals leads to the formation of sandwich compounds, in which the tetranuclear hydroxo complex is located between two macrocyclic molecules. The polynuclear complexes are additionally stabilized by the chelating effect of the isonicotinate ligands generated by hydrolysis of 4-cyanopyridine. In the complexes, the aromatic moiety of the isonicotinate ion is encapsulated into the hydrophobic inner cavity of cucurbit[6]uril. In the absence of cucurbit[6]uril, the reaction with 4-cyanopyridine produces only the polymeric complexes $[\text{Nd}(\text{C}_5\text{NH}_4\text{COO})_3(\text{H}_2\text{O})_2]$ and $[\text{Ln}(\text{C}_5\text{NH}_4\text{COO})_2(\text{H}_2\text{O})_4]\text{NO}_3$ ($\text{Ln} = \text{Pr}, \text{Sm}, \text{or Gd}$), whose structures were established by X-ray diffraction. In water and aqueous solutions of nonionic and cationic surfactants, irreversible changes of the tetranuclear fragment of the complex ($\text{Ln} = \text{Gd}$) were observed after storage for two days, whereas the anionic surfactant stabilizes the complexes. © 2006 Springer Science+Business Media, Inc.

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Keywords

Aqua complexes, Crystal structure, Cucurbit[6]uril, Lanthanides