Incorporation of trinuclear lanthanide(III) hydroxo bridged clusters in macrocyclic frameworks.

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Streszczenie

A cluster of lanthanide(III) or yttrium(III) ions, $Ln_3(\mu_3\text{-}OH)_2$, (Ln(III) = Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Yb(III), or Y(III)) can be bound in the center of a chiral macrocyclic amines H_3L1^R, H_3L1^S, and H_3L2^S obtained in a reduction of a 3 + 3 condensation product of (1*R*,2*R*)- or (1*S*,2*S*)-1,2-diaminocyclohexane and 2,6-diformyl-4-methylphenol or 2,6-diformyl-4-*tert*butylphenol. X-ray crystal structures of the Nd(III), Sm(III), Gd(III), Dy(III), and Y(III) complexes reveal trinuclear complexes with Ln(III) ions bridged by the phenolate oxygen atoms of the macrocycle as well as by μ_3-hydroxo bridges. In the case of the Nd(III) ion, another complex form can be obtained, whose X-ray crystal structure reveals two trinuclear macrocyclic units additionally bridged by hydroxide anions, corresponding to a $[Ln_3(\mu_3\text{-}OH)]_2(\mu_2\text{-}OH)_2$ cluster encapsulated by two macrocycles. The formation of trinuclear complexes is confirmed additionally by ^{1}H NMR, electrospray ionization mass spectrometry (ESI MS), and elemental analyses. Titrations of free macrocycles with Sm(III) or Y(III) salts and KOH also indicate that a trinuclear complex is formed in solution. On the other hand, analogous titrations with La(III) salt indicate that this kind of complex is not formed even with the excess of La(III) salt. The magnetic data for the trinuclear Gd(III) indicate weak antiferromagnetic coupling (J = −0.17 cm^{-1}) between the Gd(III) ions. For the trinuclear Dy(III) and Tb(III) complexes the $\chi_M T$ vs T plots indicate a more complicated dependence, resulting from the combination of thermal depopulation of m_J sublevels, magnetic anisotropy, and possibly weak antiferromagnetic and ferromagnetic interactions.

Adres publiczny

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