Trinuclear and hexanuclear lanthanide(III) complexes of the chiral 3+3 macrocycle: X-ray crystal structures and magnetic properties.

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Streszczenie

A new triphenolic hexaaza chiral macrocyclic amine L forms trinuclear complexes **1–3** with rare earth metal lanthanide(III) ions (Ln = Dy, Eu, and Y) with the general formula $[Ln_3L(\mu_3\text{-}OH)_2(NO_3)_4(H_2O)_2]\cdot x CH_3OH$. The crystal structures of the nitrate derivatives of this type reveal the presence of a $\{Ln_3(\mu_3\text{-}OH)_2\}$ core within the macrocycle. For the chloride derivative of dysprosium(III) **4**, a duplex of the trinuclear compound is formed to give the hexanuclear $[Dy_6L_2(\mu_3\text{-}OH)_3(\mu_3\text{-}O)(\mu_2\text{-}Cl)_3Cl_4(H_2O)_2]$ compound, in which two trinuclear macrocyclic units are linked by bridging chloride anions, supplemented by a hydrogen bond connecting the central oxo and hydroxo bridges as well as by weak interactions at the periphery of the macrocycle. The nuclear magnetic resonance spectra of these complexes reveal a dynamic behavior in solution related to exchange of axial ligands and hindered rotation of phenyl substituents. Magnetic studies of the nitrate (**1–3**) and chloride (**4**) dysprosium(III) complexes suggest the presence of weak ferromagnetic interactions between neighboring metal centers. The interaction is strongest for compound **1**, and for the related duplex compound **4**, it appears to be somewhat weaker. The ac susceptibility measurements for complexes **1** and **4** confirm their field-induced single-molecule magnet behavior with the following characteristics: U_{eff} = 10.6 cm^{-1} (15.2 K), $\tau_0 = 2.05 \times 10^{-4}$ s under 2500 Oe dc fields for **1**; U_{eff} = 7.9 cm^{-1} (11.4 K), $\tau_0 = 1.68 \times 10^{-4}$ s under a 3000 Oe dc field for **4**.

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https://www.acs.org/content/acs/en.html