Triple-Decker Hexaazamacrocyclic Lanthanide(III) Complexes: Structure, Magnetic Properties, and Temperature-Dependent Luminescence

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Streszczenie

The reaction of fluoride anions with mononuclear rare-earth(III) complexes of the hexaazamacrocycle derived from 2,6-diformylpyridine and ethylenediamine affords trinuclear coordination compounds **$[Ln_3L_3(\mu_2\text{-}F)_4(NO_3)_2](NO_3)_3$**. The X-ray crystal structures of these complexes show triplex cationic complexes where the three roughly parallel macrocyclic lanthanide(III) units are linked by bis-μ_2-F bridges. The detailed analysis of the photophysical properties of the **$[Eu_3L_3(\mu_2\text{-}F)_4(NO_3)_2](NO_3)_3\cdot 2H_2O$** and **$[Tb_3L_3(\mu_2\text{-}F)_4(NO_3)_2](NO_3)_3\cdot 3H_2O$** complexes reveals different temperature dependence of luminescence intensity and luminescence decay time of the Eu(III) and Tb(III) derivatives. The spectra of mixed species of average composition **$[Eu_{1.5}Tb_{1.5}L_3(\mu_2\text{-}F)_4(NO_3)_2](NO_3)_3\cdot 3H_2O$** are in accordance with the ratiometric luminescent thermometer behavior. Measurements of the direct-current (dc) magnetic susceptibility of the **$[Dy_3L_3(\mu_2\text{-}F)_4(NO_3)_2](NO_3)_3\cdot 2H_2O$** complex indicate possible ferromagnetic interactions between the Dy(III) ions. Alternating current (ac) susceptibility measurements of this complex indicate single-molecule magnet behavior in zero dc field with magnetic relaxation dominated by Orbach mechanism and an effective energy barrier U_{eff} = 12.3 cm^{-1} (17.7 K) with a pre-exponential relaxation time, τ_0 of 7.3 × 10^{-6} s. A similar reaction of mononuclear macrocyclic complexes with a higher number of fluoride equivalents results in polymeric **$\{[Ln_3L_3(\mu_2\text{-}F)_5](NO_3)_4\}_n$** complexes. The X-ray crystal structure of the Nd(III) derivative of this type shows trinuclear units that are additionally linked by single fluoride bridges to form a linear coordination polymer.

Słowa kluczowe

Anions, Ions, Ligands, Macrocycles, Magnetic Properties

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