Cyclic and linear structures constructed by ionic bonds between alkali ion and pinwheel pentanuclear $[Gd^{III}(Cu^{II}L)_4]$ core of M $[Gd^{III}(Cu^{II}L)_4]$ (M^+ = Na^+, K^+, and Cs^+; H_3L = *N*-(4,-methyl-6-oxo-3-azahept-4-enyl)oxamic acid).

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Streszczenie

Three copper(II)gadolinium(III) complexes M[Gd(CuL)4] with M+ = Na+, K+, and Cs+ have been synthesized, where H3L denotes N-(4-methyl-6-oxo-3-azahept-4-enyl) oxamic acid. The anionic part [Gd(CuL)4]- assumes a pinwheellike pentanuclear GdCu4 core and the central GdIII ion is coordinated by eight oxygen atoms of four "(CuL)," where each "(CuL)" assumes a square-planar N2O2 coordination geometry and functions as a bidentate chelate ligand to Gd III ion. The sodium and potassium salts assume a one-dimensional (1D) chain structure bridged by Na+ or K+ ions, while the cesium salt assumes a cyclic dimeric structure bridged by Cs+ ions. For the assembly structures, the cation acts as a connector between adjacent [Ln(CuL)4]- cores. The magnetic data demonstrated an intracluster ferromagnetic interaction between GdIII and Cu II ions within a GdCu4 core and an intercluster antiferromagnetic interaction through the cation. The magnetic susceptibilities can be reproduced by the spin Hamiltonian based on the pentanuclear GdCu 4 structure, Ĥ = βH(4gCuSCu + g GdSGd) - 2JSGd(SCu1 + S Cu2 + SCu3 + SCu4). The best-fit parameters are gGd = 2.00, gCu = 2.12, JGd-Cu =+1.11 cm -1, zJ' = -0.065 cm-1, and 0.4% of monomeric Cu II impurity for the Na+ salt,; gGd = 2.00, gCu = 2.13, JGdCu=+ 1.03 cm-1, zJ' = -0.038 cm-1, and 0.2% of monomeric CuII impurity for the K + salt,; and gGd = 2.00, gCu = 2.14, J GdCu=+ 0.67 cm-1, zJ' = -0.025 cm-1, 0.2% of monomeric CuII impurity for the Cs+ salt. The Gd-Cu coupling constant J is very similar in the Na+ and K+ salts (+1.11 and +1.03 cm-1) but is slightly smaller for the Cs + salt (+0.67 cm-1), probably due to the different packing of the GdCu4 clusters in the latter salt (cyclic dimers instead of an infinite chain); (2) the intercluster antiferromagnetic interaction, responsible for the low temperature decrease of XMT, significantly decreases when the ionic radius of the alkali cation increases (Na+ > K+ > Cs+) thus keeping the pentanuclear units further apart.

Adres publiczny

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