Synthesis and magneto-structural studies on a new family of carbonato bridged 3d–4f complexes featuring a [Co_3^{II} Ln_3^{III} (CO_3)] (Ln = La, Gd, Tb, Dy and Ho) core: slow magnetic relaxation displayed by the cobalt(II)–dysprosium(III) analogue.

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Streszczenie

A new family of [3 + 3] hexanuclear 3d–4f complexes [(μ_3-CO_3){$Co^{II}Ln^{III}L(\mu_3$-OH)(OH_2)}$_3$]-(ClO_4)·*m*C_2H_5OH·*n*H_2O (**1–5**) [Ln = La (**1**), Gd (**2**), Tb (**3**), Dy (**4**), and Ho (**5**)] have been prepared in moderate to high yields (62–78%) following a self-assembly reaction between the ligand 6,6′,6″-(nitrilotris(methylene))tris-(2-methoxy-4-methylphenol) (H_3L), $Co(OAc)_2$·$4H_2O$ and the lanthanide ion precursors in the mandatory presence of tetrabutylammonium hydroxide. During the reaction, atmospheric carbon dioxide is fixed in the product molecule as a bridging carbonato ligand which connects all the three lanthanide centers of this molecular assembly through a rare η^2:η^2:η^2–μ_3 mode of bridging as revealed from X-ray crystallography. The metal centers in all these compounds, except the Gd^{III} analogue (**2**), are coupled in antiferromagnetic manner while the nature of coupling in the $Co^{II}_3Gd^{III}_3$ complex is ferromagnetic. DFT calculations revealed that this ferromagnetic interaction occurs most likely by the Co^{II}–Gd^{III} superexchange, mediated *via* the bridging oxygen atoms. Only the Co^{II}–Dy^{III} compound (**4**) displayed a slow relaxation of the magnetization at a very low temperature as established by AC susceptibility measurements. The data provides an estimation of the activation energy U/k_B = 9.2 K and the relaxation time constant $\tau_0 = 1.0 \times 10^{-7}$ s.

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