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End-to-end azides as bridging ligands in lanthanide coordination chemistry: Magnetic and Magnetocaloric Properties of Tetranuclear Ln_4 ($\text{Ln} = \text{Gd}, \text{Dy}$) complexes exhibiting a rare rhombus topology

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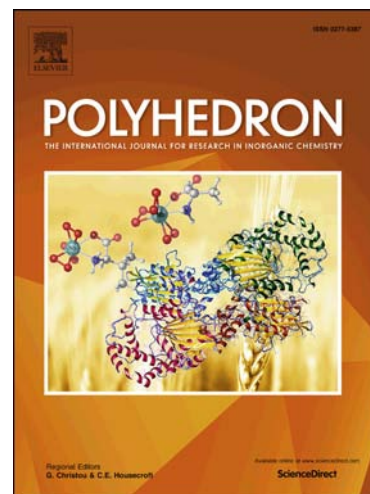
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Magnetic and Magnetocaloric Properties of Tetranuclear Ln_4 ($\text{Ln} = \text{Gd}, \text{Dy}$)
complexes exhibiting a rare rhombus topology**

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Abstract

The synthesis and magnetic properties of two new isostructural tetranuclear lanthanide complexes, $[\text{Ln}_4(\text{N}_3)_4(\text{Tpz})_8]$ ($\text{Ln} = \text{Gd}^{\text{III}}$ (**1**), Dy^{III} (**2**), and $\text{Tpz} = \text{tris(pyrazolyl)borate}$) are reported. In these complexes the lanthanide ions are eight coordinate with distorted geometries and are bridged by end-to-end azido ligands in a rare rhombus topology. Direct current magnetic susceptibility studies revealed the presence of weak ferromagnetic exchange interactions between the metal ions which were quantified in the case of the isotropic Gd_4 analogue to give $J = 0.0080(2) \text{ cm}^{-1}$ and $g = 2.01(1)$. Complex **2** exhibits frequency and temperature dependent out-of-phase (χ'') *ac* magnetic susceptibility signals under a 0.1 T applied field, suggestive of SMM behavior. Low temperature magnetization studies revealed that compound **1** exhibits an appreciable magnetic entropy change, $-\Delta S_m$, which reaches a value of $\sim 20.9 \text{ J kg}^{-1} \text{ K}^{-1}$ at $T = 3 \text{ K}$ for $\Delta H = 7 \text{ T}$. Theoretical calculations further support the experimental results.

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