Building 1D lanthanide chains and non-symmetrical [Ln_2] "triple-decker" clusters using salen-type ligands: magnetic cooling and relaxation phenomena.

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Rok wydania

2016

Czasopismo

Dalton Transactions

Numer woluminu

45

Strony

18591-18602

DOI

10.1039/c6dt02932a

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

A solvothermal reaction between $Ln(NO_3)_3{\cdot}6H_2O$ (Ln: Gd, Tb and Dy), 2-hydroxy-1-naphthaldehyde, 2-OH-naphth, and ethylenediamine, en, in MeOH in the presence of a base, NEt_3, led to the formation of the 1D coordination polymers $[Ln(L)(MeO)(MeOH)_{0.5}]_n{\cdot}MeOH$ (Ln = Gd (**1**·MeOH), Tb(**2**), Dy (**3**·MeOH); H_2L = 1,1′-((1*E*,1′*E*)-(ethane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(naphthalen-2-ol), the Schiff-base ligand derived from the condensation of 2-OH-naphth and en), while a similar reaction in an excess of NaN_3 yielded 1D coordination polymers $[Ln(L)(N_3)_{0.75}(MeO)_{0.25}(MeOH)]_n$ (Ln = Gd (**4**), Tb (**5**), Dy (**6**)). Finally, upon replacing ethylenediamine with *o*-phenylenediamine, *o*-phen, we managed to isolate the discrete dimers $[Dy_2(L')_3(MeOH)]{\cdot}2MeOH$ (**7**·2MeOH) and $[Gd_2(L')_3(MeOH)]{\cdot}2MeOH$ (**8**·2MeOH) (H_2L' = 1,1′-((1*E*,1′*E*)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(naphthalen-2-ol), the Schiff-base ligand from the condensation of 2-OH-naphth and *o*-phen). Polymers **1–3** describe one-dimensional chains, containing alternating seven- and eight-coordinate Ln^{III} metal centers, polymers **4–6** contain eight-coordinate lanthanide ions, while in both **7** and **8** the two Ln^{III} centers are eight- and seven-coordinate, adopting square antiprismatic and “piano-stool” geometry, respectively. The magnetocaloric properties of the three Gd^{III} analogues were determined from magnetic measurements, yielding the magnetic entropy change $-\Delta S_m$ = 21.8, 23.0 and 16.0 J kg^{-1} K^{-1} at T = 3.0 K on demagnetization of 7 T to 0, for **1**, **4** and **8**, respectively. The study of the magnetic properties also revealed that all three Dy^{III} analogues (**3**, **6** and **7**) display out-of-phase signals, therefore suggesting slow magnetic relaxation, while such behaviour was not established in the Tb^{III} analogues.