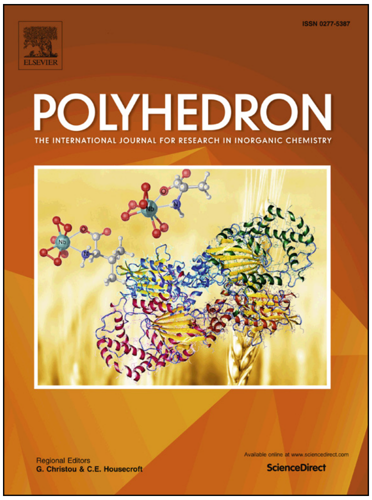

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A family of $Fe^{III}_4Ln^{III}_4$ clusters containing derivatised salicylaldoximate ligand: syntheses, structures and magnetic properties

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Abstract

A family of octanuclear clusters $[Fe^{III}_4Ln^{III}_4O_2(OH)_4(mosaoH)_4(Piv)_4(N\text{-}mdea)_4(H_2O)_2]$ [Ln = Y(**1**), Gd(**2**), Tb(**3**) and Dy(**4**), $mosaoH_2$=3-Methyloxysalicylaldoxime, N-$mdeaH_2$ = N-methyl diethanolamine, pivH = pivalic acid] have been prepared by reactions of $[Fe_3O(piv)_6(OH_2)_2(OH)]\cdot H_2O$ with $Ln(NO_3)_3\cdot 6H_2O$, $mosaoH_2$ and N-$mdeaH_2$ ligands . The crystal structures of **1**–**4** were obtained, and their core can be described as two distorted tetrahedral subunits of $[Fe_2Ln_2(\mu_4–O)]$ connected by a pair of $\mu_3–OH^–$ groups. A dc magnetic susceptibility study reveals that there exists strong antiferromagnetic interactions between the neibouring Fe atoms. Fitting of the susceptibility data of compound **1** containing diamagnetic Y^{III} ions gives $J = –127\ cm^{–1}$. Compound **4** exhibits frequency-dependent out-of-phase ac susceptibility signals indicative of slow magnetization relaxation.

Keywords

Fe-Ln heterometallic clusters; syntheses; structures; magnetic properties.

Introduction

Recent years have witnessed intense and growing interests towards single-molecule-magnets (SMMs) due to their unique magnetic properties and potential applications in information storage or quantum computing[1-6]. SMMs are molecules that can function as nanoscale magnets below a certain blocking temperature (T_B) as they have a significant energy barrier to reversal of the magnetization vector, which originates from the combination of a large ground-state spin and a significant uniaxial (Ising) magnetic anisotropy[7-8]. 3d-4f system has recently received great attention as a promising candidate for probing new SMMs, since they could incorporate the favorable properties of both types of ions and exhibit interesting magnetic behavior. As the cheaply and readily available metal source, high spin Fe^{III} ions combined with highly anisotropic lanthanide ions towards Fe/Ln clusters would probably meet the requirements of SMMs and find wide applications in magnetic devices. Several explorations have generated Fe^{III}/Ln SMMs of various nuclearities, including $Fe_{12}Sm_4$[9], Fe_6Dy_3[10], Fe_2Dy_4[11], Fe_2Dy_3[12], Fe_2Dy_2[13-14], Fe_4Dy_4[15], Fe_4Dy_2[16-17], Fe_7Dy_3[18] and etc. Their structures have various core topologies, in which cubane and defect double-cubane units are relatively common, as could be found in $Fe_{12}Sm_4$, Fe_4Ln_2, Fe_2Ln_4 and Fe_2Ln_2 compounds. And other core types include the cone-like Fe_6Dy_3, the square pyramid Ln_3Fe2, the ring-like Fe_4Dy_4, the S-shape Fe_4Dy_4 and etc. The metal ions are held together mostly by oxygen group, and the Fe-O bond lenth and Fe-O-Fe angle have great effects on the magnetic interaction between the Fe centers. It could be found that the majority of the Fe^{III}/Ln SMMs reported is Fe^{III}/Dy compounds. As is pointed out by Powell A. K. *et. al*, the peculiar anisotropy of Dy^{III} ions should be responsible for the presence of slow magnetic relaxation.

3-Methyloxysalicylaldoximate ligand, containing the weakly coordinating methoxy group which may specifically bind to the Ln^{III} ions, as well as the phenolic group and oximate group, is expected to have the potential to coordinate to both 3d and 4f ions. However, this ligand is less explored to date[19-21], especially in 3d/4f system, with the only case of a family of Mn_3Ln_4[22] clusters recently reported by our group, which display slow magnetic relaxation. Therefore, we extended the study of this ligand to Fe-Ln system and isolated a family of octanuclear Fe_4Ln_4 clusters. Here we describe the syntheses, structures,