Structure and Magnetic Properties of Three-Dimensional Gadolinium-Based Hybrid Framework

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In the present work we have focused on the preparation and magnetic study of coordination polymer formed by gadolinium(III) cations as nodes and formate (HCOO −; FOR) anions as charge compensating linkers. The prepared complexes with formula \( \{[Gd(\mu_3-\text{FOR})_3]_n \} \), where Ln(III) = La, Ce, Pr, Nd, Sm, Eu, and Gd; FOR = formate, were characterized by single-crystal X-ray diffraction, and high-energy powder X-ray diffraction. The structural study showed that complex is formed by 3D polymeric network with the shortest Gd-Gd, distances of 3.998 Å. The magnetic properties of the complex were studied by magnetic susceptibility \( \chi(M) \) and magnetization \( M(H) \) measurements. The results show the weak antiferromagnetic coupling at low temperatures represented by the Weiss constant \( \theta \approx -0.468 \) K. The value of effective magnetic moment \( \mu_{\text{eff}} = 7.57 \mu_B \) which was estimated from the experimental data is close to the theoretical value for systems with \( S = 7/2 \).

The stability of the polymeric framework was investigated using HE-XRD measured during in-situ heating to 600 °C with temperature step of 10 °C. The phenomena suggest that framework of the compound is stable in temperature range 20–410 °C. Above 410 °C the intensities of the strongest diffraction peak centred on monocromatic MoKα irradiation (\( \lambda = 0.71073 \) Å) on a four-circle \( \kappa \)-axis Xcalibur2 diffractometer equipped with a detector Sapphire2 (Oxford Diffraction).

High energy X-ray diffraction (HE-XRD) measurements were carried out with wiggler beamline BW5 in DESY (Hamburg, Germany). Diffractions photons were collected using two-dimensional image plate square detector Perkin-Elmer 1621 with a pixel size 150×150 μm². Magnetic properties were investigated using a SQUID (Superconducting Quantum Interference Device) apparatus in the external dc field up to 5 T and in the temperature range of 2–300 K.

1. Introduction

During the last decade, polymeric metal complexes have attracted considerable interest because of their structural diversity as well as their potential applications in practical areas, such as catalysis, gas storage and magnetism [1, 2]. Large number of unpaired electrons in some rare earth elements, i.e. high angular spin momentum, makes the 4f cations ideal candidates for preparation of compounds with desired and interesting magnetic properties. Complexes built from 4f metal carboxylates should be of special interest for the study of magnetic exchange interactions through the bridging carboxylate groups [3].

In our work, we have solvothermally prepared series of isomorphous three-dimensional coordination polymers with formula \( \{[Ln(\mu_3-\text{FOR})_3]_n \} \), where Ln(III) = La, Ce, Pr, Nd, Sm, Eu, and Gd; FOR = formate. The compounds were characterized by elemental analysis, IR and Raman spectroscopy, thermogravimetry, single-crystal X-ray diffraction and high-energy X-ray diffraction. For the gadolinium compound, which has largest spin angular momentum (\( S = 7/2 \)), the magnetic properties were investigated by SQUID apparatus. The results of structural and magnetic studies of \( \{[Gd(\mu_3-\text{FOR})_3]_n \} \) are described in this paper.

2. Experimental

The complex \( \{[Gd(\mu_3-\text{FOR})_3]_n \} \) was synthesised under solvothermal conditions in teflon lined Parr® autoclaves using DMF solvent. The single-crystal X-ray reflection intensities were collected at 170 K with graphite monochromatic MoKα irradiation (\( \lambda = 0.71073 \) Å) on a four-circle \( \kappa \)-axis Xcalibur2 diffractometer equipped with a detector Sapphire2 (Oxford Diffraction).

The crystal structure of the complex is shown in Fig. 1. The structure of \( \{[Gd(\mu_3-\text{FOR})_3]_n \} \) can be characterized as a three-dimensional (3D) neutral framework (space group \( R3m \)) composed of Gd(III) cations as nodes and formate anions as linkers. The Gd(III) atoms lie on a site of \( R3 \) symmetry and are coordinated by nine O atoms from nine different formate groups. The coordination polyhedron around Gd(III) can be described as an ideal three-capped trigonal prism. Each C atom makes three C-O-Gd linkages through one \( \mu_2 \)-bridging O atom (O2) and one \( \mu_3 \)-bond O atom (O1) (see Fig. 1a). The Gd-O1 bond distance is 2.502(2) Å, while the respective distances for bridging oxygen (O2) are 2.580(1) and 2.597(1) Å. Three Gd ions are interconnected by three formate anions and form six-membered rings in framework (Fig. 1b). The shortest Gd-Gd distance is 3.998 Å.

The stability of the polymeric framework was investigated using HE-XRD measured during in-situ heating to 600 °C with temperature step of 10 °C. The phenomena suggest that framework of the compound is stable in temperature range 20–410 °C. Above 410 °C the intensities of the strongest diffraction peak centred...
at 11.9 nm\(^{-1}\) decreased with increasing temperature, indicating decomposition of the compound. Above 430 °C the framework totally collapsed and formation of Gd\(_2\)O\(_3\) as final decomposition product was observed.

The temperature dependence of the magnetic susceptibility was investigated by SQUID apparatus. The molar magnetic susceptibility \(\chi_M\) of the sample slowly increased with decreasing temperature, as shown in Fig. 3. The \(\chi_M\) follows the Curie-Weiss law with a Curie constant of 7.193 Kemu mol\(^{-1}\) and a negative Weiss constant \(\theta = -0.468\) K in the temperature region from 2 to 300 K (inset in Fig. 3), showing on the weak antiferromagnetic interactions in the complex. Also, the \(\chi_M T\) value decreases from 7.15 cm\(^3\) K mol\(^{-1}\) at 300 K to 5.86 cm\(^3\) K mol\(^{-1}\) at 2 K, which is indicative of antiferromagnetic exchange interactions in the compound [4].

Conclusions

Novel three-dimensional gadolinium-based hybrid framework was prepared. The magnetic Gd(III) cations in the frameworks (\(S = 7/2\)) are interconnected by short, formate linkers. The magnetic studies of prepared system showed on the antiferromagnetic exchange coupling represented by Weiss constant of \(\theta = -0.468\) K. The calculated value of effective magnetic moment \(\mu_{\text{eff}} = 7.57\mu_B\) was estimated from the experimental data. The detailed analysis of paths of the magnetic exchange interactions, using theoretical models, will be performed in the near future.

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