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 Gd(III) cations as nodes and formate ($HCOO^-$; FOR) anions as charge compensating linkers. The prepared complex with formula $\{[Gd(\mu_3-FOR)_3]\}_n$ was 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 $\chi_M(T)$ and magnetization $M(H)$ measurements. The results show on the weak antiferromagnetic coupling at low temperatures represented by the Weiss constant $\theta = -0.468$ K. The value of effective magnetic moment $\mu_{eff} = 7.57\mu_B$, which was estimated from the experimental data is close to the theoretical value for systems with $S = 7/2$. Correlation between crystal structure of complexes and magnetic properties is presented.

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 solvothermaly prepared series of isomorphous three-dimensional coordination polymers with formula $\{[Ln(\mu_3-FOR)_3]\}_n$, (were Ln(III)= La, Ce, Pr, Nd, Sm, Eu, 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 $\{[Gd(\mu_3-FOR)_3]\}_n$ are described in this paper.

2. Experimental

The complex $\{[Gd(\mu_3-FOR)_3]\}_n$ 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 MoK_α irradiation ($\lambda = 0.71073$ Å) on a four-circle κ-axis Xcalibur2 diffractometer equipped with a detector Sapphire2 (Oxford Diffraction).

High energy X-ray diffraction (HE-XRD) measurements were carried out at wiggler beamline BW5 in DESY (Hamburg, Germany). Diffracted photons were collected using two-dimensional image plate square detector Perkin-Elmer 1621 with a pixel size 150×150 μm^2.

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.

3. Results and discussion

The crystal structure of the complex is shown in Fig. 1. The structure of $\{[Gd(\mu_3-FOR)_3]\}_n$ 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 μ_2-bridging O atom (O2) and one μ_1-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 patterns demonstrate that framework of the compound is stable in temperature range 20–410 °C. Above 410 °C the intensities of the strongest diffraction peak centred

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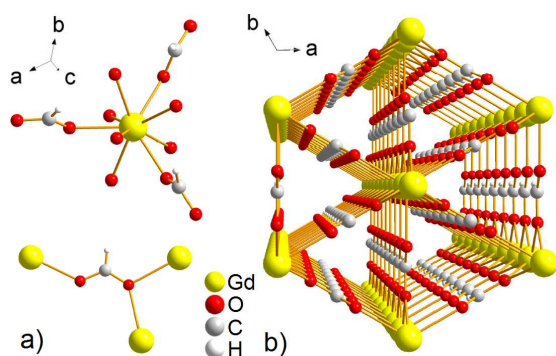*corresponding author; e-mail: miroslav.almasi@upjs.sk, vladimir.zelenak@upjs.sk

Fig. 1. a) Coordination environment around Gd(III) cations and FOR anions. b) View on the 3D framework of $\{[Gd(\mu_3-FOR)_3]\}_n$.

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_2O_3 as final decomposition product was observed.

The temperature dependence of the magnetic susceptibility was investigated by SQUID apparatus. The molar magnetic susceptibility χ_M of the sample slowly increased with decreasing temperature, as shown in Fig. 3. The χ_M follows the Curie-Weiss law with a Curie constant of 7.193 K emu 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].
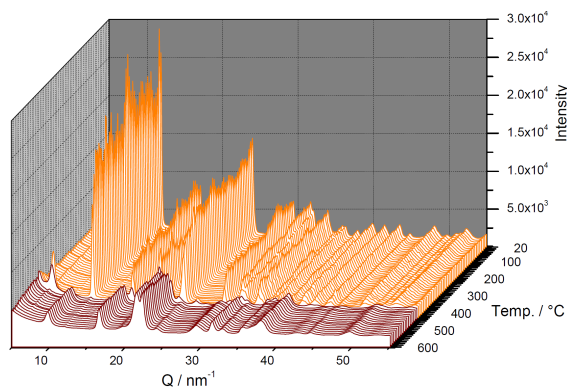

Fig. 2. HE-XRD diffraction patterns of $\{[Gd(\mu_3-FOR)_3]\}_n$ measured during *in-situ* heating.

The experimental data of magnetization vs. magnetic field ($M(H)$ loops; not shown) were characterized by upward curvature at 2 K. This behaviour at low temperatures suggests that interactions in the material might

be relatively strong. The magnetization data were compared with the Brillouin function describing an $S = 7/2$ paramagnet. Such comparison showed on the presence of antiferromagnetic coupling, since the total magnetization at a given magnetic field was significantly smaller when compared with the prediction for paramagnetic system.
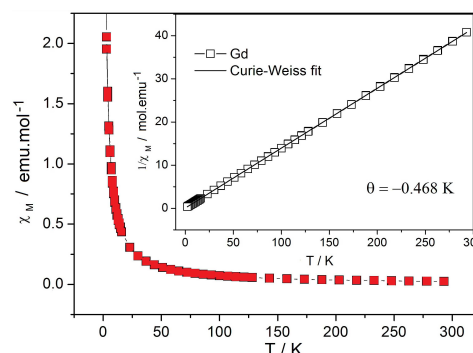

Fig. 3. Molar magnetic susceptibility of polymer complex $\{[Gd(\mu_3-FOR)_3]\}_n$, inset the Curie-Weiss fit.

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 $\mu_{eff} = 7.57\mu_B$ 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.

References

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