



Molecular paramagnets. The effect of structural modification on (porphyrinato) gadolinium(III) magnetothermal properties



Victor V. Korolev, Tatyana N. Lomova*, Anna G. Ramazanova, Elena G. Mozhzhukhina

G. A. Krestov Institute of Solution Chemistry of the Russian Academy of Sciences, 153045 Ivanovo, Russian Federation

ARTICLE INFO

Article history:

Received 19 April 2016

Received in revised form 27 June 2016

Accepted 19 July 2016

Available online 29 July 2016

Keywords:

Porphyrins

Rare earths

Magnetothermal properties

Magnetocaloric effect

Structure effect

ABSTRACT

Depending on an axial ligand, paramagnetic rare earth porphyrin complexes show the magnetocaloric effect changed from 0.127 to 1.45 K (“great magnetocaloric effect”) at the temperatures close to room when the magnetic field changes from 0 to 1.0 T and thus are important candidates for new functional molecular materials in magnetic refrigeration and hyperthermia. Effect of extension of the π networks along axis perpendicular to the macrocycle plane due to chelating acetylacetonate anion on a magnetic behaviour of gadolinium(III) porphyrin is presented in this work. Magnetothermal properties namely a specific heat capacity, a magnetocaloric effect, a heat released due to magnetocaloric effect, an enthalpy/entropy change of magnetization of 2.5% water suspensions of (5,10,15,20-tetraphenyl21H,23H-porphinato) gadolinium(III) acetylacetonate, (Acac)(AcacH)₃GdTPP are studied as a function of both temperature and magnetic induction. Direct methods of the microcalorimetry and differential scanning calorimetry were used for the measuring of a magnetocaloric effect and a specific heat capacity, respectively. The effect of axial acetylacetonate on magnetothermal properties is discussed in comparison with the data for the axial acetate and chloride complexes in a view of optimization of magnetothermal properties for application in cooling and hyperthermia.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The implementation of the magnetocaloric effect (MCE) can successfully replace the vapor-compression cycle in refrigerators or air-conditioning units [1]. The use of MCE in a medicine (for hyperthermia) is the second promising direction in magnetochemistry [2–5]. Development of these areas in science and engineering is promoted by design and synthesis of the compounds with paramagnetic properties. As all paramagnets exhibit MCE, a search the compounds with the large and giant MCE is very important.

The europium, thulium, and gadolinium complexes with 5,10,15,20-tetraphenyl21H,23H-porphine (H₂TPP) and acetate or chloride as axial ligand was recently found [6,7] to display MCE of 0.127–1.45 K (“great magnetocaloric effect” [8–10]) at temperatures close to room. It was shown that effect of an axial ligand on magnetothermal properties of the complexes prevails over similar effect of a central lanthanide ion. (5,10,15,20-Tetraphenyl21H,23H-porphinato) gadolinium(III) acetylacetonate, (Acac)LnTPP as the complex with large conjugated macrocycle plane and with the

possibility of the extension of the π conjugation system along the axial axis is of great interest. Magnetic behavior of rare earth complexes is determined by the ligand field around a lanthanide ion [11–13] due to the strong electronic repulsion leading to the maximizing of the spin and orbital atomic moment. The magnetic coupling mechanism operating through metal ligation has been used successfully in designing a potential molecular system with magnetic behavior. A number of mechanisms based on hydrogen bonds [14], conjugated π systems [15,16] and coupling of spin-containing units with a ferromagnetic coupling unit [17] are already well known. The intramolecular π interactions in (Acac)LnTPP between lanthanide ion and macrocyclic or axial π ligands due to dative π bonds metal-ligand are also possible.

We suppose, that (5,10,15,20-tetraphenyl21H,23H-porphinato) gadolinium(III) acetylacetonate with the composition (Acac)(AcacH)₃GdTPP reported herein is promising as molecular paramagnets in magnetic refrigeration near room temperature and in hyperthermia.

In this work, we studied magnetothermal properties of (5,10,15,20-tetraphenyl21H,23H-porphinato) gadolinium(III) acetylacetonate (Fig. 1) as 2.5% water suspensions at 278–318 K in a magnetic induction of 0–1.0 T. Three molecules of acetylacetonate (AcacH) coordinating by the donor-acceptor bonds are omitted in

* Corresponding author.

E-mail addresses: tnl@isc-ras.ru, tnl50@mail.ru (T.N. Lomova).

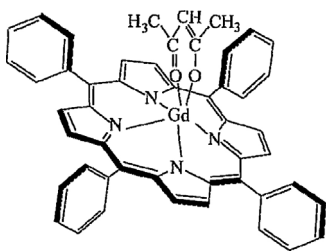


Fig. 1. Chemical structure of (5,10,15,20-tetraphenyl-21H,23H-porphinato) gadolinium(III) acetylacetonate, (Acac)GdTPP.

Fig. 1 and in the abbreviation for complex below. We obtained MCE, a heat released due to MCE, specific heat capacity, and an enthalpy/entropy change of magnetization as a function of temperature and magnetic induction. We showed that modifications of the axial position in a porphyrin complex are a promising method to achieve MCE parameters for practical applications.

2. Experimental

2.1. Synthesis and characterization

Synthesis of (Acac)GdTPP was performed by the reaction of H_2TPP (0.02198 g) with $Gd(Acac)_3$ (0.05059 g) in boiling imidazole (5 g). The reaction was finished after one hour. The monitoring for reaction completion was carried by the disappearance of the porphyrin absorption bands (λ_{max} , nm (log ϵ , $CHCl_3$): 648 (3.65), 592 (3.75), 551 (3.89), 516 (4.26), 420 (5.43), 373 (4.37)) in the UV–vis spectrum of the reaction mixture contributed in chloroform. The reaction mixture was cooled, dissolved in chloroform and purified from imidazole by repeated washing with water. The solution of complex in chloroform was concentrated and chromatographed on an alumina column (Brockmann activity grade II) using first chloroform than ethanol –1% AcOH mixture. Yield is 20%. UV–vis spectrum (CH_2Cl_2) λ_{max} , nm: 593, 553, 516, 494, 423. IR (KBr) ν , cm^{-1} : vibrations of pyrrol cycles, 799 (γ C–H); 987, 1006 (ν C–C), (ν C–N, δ C–H); 1328 (ν C–N); and 1440 (ν C=N); vibrations of benzene cycles, 702, 752 (γ C–H); 1069, 1177 (δ C–H); 1491, 1575, 1596 (ν C=C); and 3021, 3053 (ν C–H); bond vibrations of axial ligand $Acac^-$, 1516 (ν C=O); 1262, 1273 (ν C–CO–C); 1402 (δ_s C–H, CH_3), 1491 (δ_{as} C–H, CH_3); 2854, 2923 (ν C–H, CH_3), 966 (δ C–H, =C₃–H); vibrations of Gd–N bonds, 423; vibrations of Gd–O bonds, 659, 724. 1H NMR ($CDCl_3$), (d: ppm): 8.87 (s, H β), 8.25 (s, H $_{ortho}$), 7.79–7.54 (m, H $_{meta}$, H $_{para}$), 5.4 (very broad singlet, CH $_{enol}$), 3.67–3.54 (ss, (CH $_2$) $_{ketone}$), 2.21 (s, (CH $_3$) $_{ketone}$), 2.0 (s, CH $_3$) $_{enol}$). MS (MALDI TOF): m/z = 1183.70 for $[M + 14H]^+$; Calcd. 1183.56; m/z = 1071.57 for $[M - (Acac) + 2H]^+$; Calcd. 1071.35; m/z = 769.18 for $[M - (Acac)(AcacH)_3]^+$; Calcd. 769.99. Found: C 66.81, H 2.91, N 5.28%. $C_{64}H_{59}N_4O_8Gd$ requires C 65.73, H 5.08, N 4.79%.

2.2. Equipment

Magnetocaloric effects of paramagnetic complex were studied using the special calorimetric device, the isothermal-shell microcalorimeter which shape and construction are developed in the work [17]. The microcalorimetric cell full of paramagnet suspension together with the isothermal shell was placed in the gap of the electromagnet. Adiabatic conditions for magnetization process were achieved by rapid magnetic field changes. The temperature fluctuation of 0.0002 °C in the thermostatically controlled calorimetric cell space during the calorimetric experiment and the setup sensitivity of 2×10^{-5} K were maintained. The error in MCE measurements that were repeated five times did not

exceed 2%. Heat capacities with an error of about 2% were measured in zero fields by means of DSC 204 F1 Phoenix (NETZSCH).

The UV–vis spectra were measured on Agilent 8453 UV–vis spectrophotometers; IR and 1H NMR spectra were recorded on a VERTEX 80v and a Bruker Avance III-500 NMR spectrometers respectively; elemental analysis was performed on a Euro EA 3000; mass spectrum was performed on Bruker Autoflex.

2.3. Suspension fabrication

Amorphous samples of (Acac)GdTPP were used for suspensions. A solid was in the highly disperse state in suspension; the average size of particles of 25 μm was controlled with polarizing microscope Altami Polar 312. A solid did not change during microcalorimetric experiment on both size of particles and chemical composition, which was confirmed by microscopy and spectrophotometry, respectively.

2.4. Calculation of the magnetothermal parameters

The amount of heat Q_{MCE} , which was allocated (when magnetic field is switched on) because of the magnetocaloric effect in paramagnets, was calculated by the Formula (1):

$$Q_{MCE} = Q_j (\Delta T / \Delta T_j), \quad (1)$$

Here Q_j – Joule heat, injected in the calorimetric experiment, ΔT_j – the temperature change of calorimetric system as result of injecting of Joule heat, ΔT – the temperature change of a calorimetric system as a result of a magnetic field change. Equation of heat balance [18] has the form (2).

$$Q_{MCE} = m_m C_{p,m} \Delta T_{MCE} \quad (2)$$

Here ΔT_{MCE} – the adiabatic temperature change that is MCE, m_m , $C_{p,m}$ – mass and heat capacity of a magnetic material.

The enthalpy change $\Delta H_{(enth)}$ of a magnetic material resulting from the changes in the magnetic field was determined from the experimental values of Q_{MCE} . The entropy values were calculated from MCE at specified values of C_p and temperature. Heat capacity in zero fields in solid of complexes was directly measured in experiment.

3. Results and discussion

Numerical MCE values for (Acac)GdTPP were obtained by the direct method of detection a temperature change in the calorimeter, which occurred as a result of the magnetocaloric effect during the microcalorimetric experiment (Experimental section). This method was used in magnetochemistry of tetrapyrrole complexes firstly in our work [19]. Effect of an axial ligand structure on the magnetothermal properties of gadolinium porphyrin was examined using the data observed in this work and preliminary ones from articles [6,7,20].

3.1. The testing of the microcalorimeter

The polycrystalline metallic gadolinium (chemical purity of 98%) as in [21–23] was taken for the check the reliability of the microcalorimetric method used. Fig. 2 shows temperature dependence of MCE in Gd when the magnetic field was changed from 0 to 1.0 T. The MCE values were obtained based on Eq. (2) (Experimental). It is known [24,25] that the temperature dependence of MCE in Gd due to magnetic phase transition has a maximum at 292 K. Experimental values of MCE, obtained by the calorimetric method, are in a good agreement with the literature

Download English Version:

<https://daneshyari.com/en/article/1440121>

Download Persian Version:

<https://daneshyari.com/article/1440121>

[Daneshyari.com](https://daneshyari.com)