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[P30] Synthesis, crystallographic characterization, magnetic and magnetocaloric properties of a nonanuclear heterometallic Cu₇Gd₂ complex

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Abstract—The synthesis, crystal structure, magnetic and magnetocaloric properties of a nonanuclear heterometallic Cu_7Gd_2 complex is discussed.

I. INTRODUCTION

Molecular magnetic materials based on homo- and/or heterometallic coordination complexes (clusters) have been extensively studied over the past decades, and have been proposed for potential applications in high-density information storage devices, quantum computing, spintronics and magnetic refrigeration [1]. The latter application requires molecules possessing a large spin ground state and negligible magnetic anisotropy and is based on the magnetocaloric effect (MCE) i.e. the isothermal change of magnetic entropy (ΔS_m) and adiabatic change of temperature (ΔT_{ad}) that follow a change of the applied magnetic field (ΔH). The upper limit for the entropy change at $T = \infty$ is $\Delta S_m = R\ln(2S+1)$, where R is the gas constant and S is the spin value. From the synthetic point of view the requirements for MCE can be achieved by the combination of 3d metal ions (to result in large spin ground state) with the isotropic Gd^{III} with $S = 7/2$ (to result in negligible magnetic anisotropy). Gd-based complexes have been studied as magnetic refrigerants with entropy change -ΔS_m up to 59 $Jkg^{-1}K^{-1}$ (at 3 K and $\Delta H = 7$ T) [2-7].

Recently we have reported the synthesis and magnetic study of the heptanuclear clusters $[Cu_5Ln_2(O_2CMe)_2(NO_3)_4(L_2)(HL)_2]$ (Ln = Gd, Tb, and $H_3L = OH-C_{10}H_7-CH=NC(C_2H_5)(CH_2OH)_2$ is a Schiff base ligand based on 2-hydroxy-1-naphthaldehyde and 2-amino-2-ethyl-1,3-propanediol). The magnetic properties of the above complexes depend on the nature of the lanthanide ion. The magnetocaloric effect of the {Gu_5Gd_2} complex was examined by isothermal magnetization studies under $\Delta H = 5$ T and showed a maximum entropy change of 15.7 $Jkg^{-1}K^{-1}$ at 2 K. The {Cu_5Tb_2} complex showed single-molecule magnet behavior in ac susceptibility measurements due to the significant anisotropy of the Tb^{III} ions [8].

We present herein our new results from the use of $Cu^{II}/Gd^{III}/H_3L$ reaction mixtures, i.e. the synthesis, crystallographic, magnetic and magnetocaloric stydies of the nonanuclear complex $[Cu_7Gd_2(piv)_4(L)_4(HL)_2(MeOH)_5]$ (piv⁻ is the monoanion of pivalic acid and $H_3L = OH-C_{10}H_7-CH=NC(C_2H_5)(CH_2OH)_2$).

II. RESULTS AND DISCUSSION

A. Synthesis and Crystallographic Characterization

The reaction of $[Cu_2(piv)_4(pivH)_2]$ with $Gd(NO_3)_4\cdot6H_2O$ and H_3L in the presence of Et_3N in MeOH gave a green solution. Green crystals of $[Cu_7Gd_2(piv)_4(L)_4(HL)_2(MeOH)_5]$ (**1**) were grown upon slow evaporation of the green reaction solution after 10 days. Complex **1** crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters ($T = 100$ K) $a = 20.0178(4)$, $b = 26.8700(5)$, $c = 25.8987(5)$ Å, $\beta = 102.574(1)$°, $V = 13596.2(5)$ Å³, $Z = 4$. Complex **1** crystallizes as **1**·4.3MeOH·0.5H₂O. The diffraction data were collected on a Rigaku R-AXIS SPIDER Image Plate diffractometer using Mo Kα radiation. Data collection (ω-scans) and processing (cell refinement, data reduction and Empirical absorption correction) were performed using the CrystalClear program pachage [9]. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares techniques on F^2 with SHELXL ver2014/6 [10]. Experimental crystallographic details: $2\theta = 54$°, reflections collected/unique/used 119776/29530 [$R_{int} = 0.0450$]/29530, 1579 parameters refined, $\Delta\sigma = 0.006$, $\Delta\rho_{max}/\Delta\rho_{min} = 1.707/-1.379$, $R1/wR2$ (26368 refs with $I>2\sigma(I)$) 0.0457/0.1176, $R1/wR2$ (all data) 0.0515/0.1210. Hydrogen atoms were included at calculated positions as riding on bonded atoms; non-H atoms were refined anisotropically.

B. Description of the Structure

Complex **1** is neutral and consists of seven Cu^{II} and two Gd^{III} ions which are held together through four L^{3-}, two HL^{2-} and two piv⁻ ligands (Figure 1). Two of the L^{3-} ligands bridge three Cu^{II} and one Gd^{III} ions and the other two L^{3-} ligands bridge two Cu^{II} and two Gd^{III} ions; all L^{3-} ligands present μ_4-κO^3:$\kappa O'^2$:$\kappa O''$:κN coordination mode. The two HL^{2-} ligands bridge two Cu^{II} and one Gd^{III} ions presenting μ_3-κO^3:$\kappa O'$:κN coordination mode. Two of the pivalate ligands brigde two Cu^{II} and one Gd^{III} ions showing the μ_3-κO^2:$\kappa O'$ mode. The remaining two pivalates are coordinated, each one around a Gd^{III} ion in the asymmetric chelate mode. The ligation of the nine metal ions is completed by five terminal MeOH molecules each one around the two Gd^{III} and three of the Cu^{II} ions.

The two Gd^{III} ions are coordinated to nine oxygen atoms with bond distances in the range 2.34-2.55 Å. The seven Cu^{II} ions show three different coordination geometries. Atoms Cu(1) and Cu(7) are coordinated to one nitrogen and three oxygen atoms

in square planar geometry with bond distances in the range 1.90-1.92 Å. Atoms Cu(2) and Cu(6) are coordinated to one nitrogen and five oxygen atoms in octahedral geometry with bond distances in the range 1.92-2.58 Å. Atoms Cu(3) and Cu(5) are coordinated to one nitrogen and four oxygen atoms in square pyramidal geometry with bond distances in the range 1.89-2.70 Å. Finally atom Cu(4) is coordinated to five oxygen atoms in square pyramidal geometry with bond distances in the range 1.90-2.42 Å.
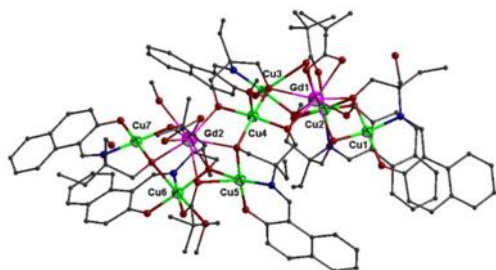
Figure 1. Partially labeled plot of the molecular structure of **1**. Color code: Gd magenta, Cu green, N blue, O red, C grey.

C. Magnetic Studies

Magnetic susceptibility measurements as a function of temperature were recorded from polycrystalline sample of **1** at 1000 Oe dc field (Figure 2). The $\chi_M T$ product for **1** at 300 K is 18.32 cm^{3}Kmol^{-1} close to the theoretical value of 18.38 cm^{3}Kmol^{-1} for seven Cu^{II} and two Gd^{III} ions. The $\chi_M T$ product remains practically unchanged down to 50 K and then increases reaching the value of 26.08 cm^{3}Kmol^{-1} at 2 K. The overall temperature dependence of the $\chi_M T$ product suggests the presence of dominant ferromagnetic interactions between the metal ions.
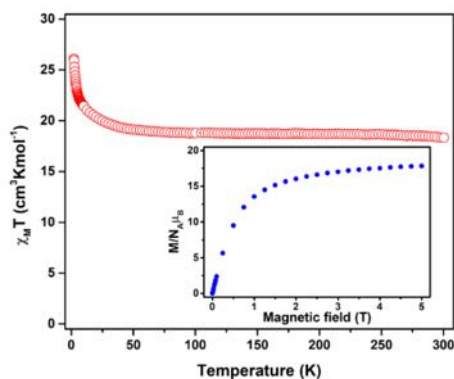

Figure 2. $\chi_M T$ vs T plot of **1** at 1000 Oe and magnetization curve at 2 K (inset).

The magnetization measurements at 2 K as a function of the external applied field show a rapid increase upon increasing of the magnetic field reaching a value of 17.84 Nμ_B at 5 T. This value is lower than the saturation value of 21 Nμ_B expected for two Gd^{III} ($S = 7/2$) and seven Cu^{II} ($S = 1/2$) ions which are uncoupled or completely ferromagnetically coupled ($S = 21/2$) suggesting that some of the metal ions are antiferromagnetically coupled.

D. Magnetocaloric Studies

The magnetic entropy changes -ΔS_m were calculated by magnetization measurements in 2-10 K range under external applied magnetic field up to 5 T (Figure 3). The -ΔS_m can be calculated from the experimental magnetization data by using the Maxwell equation

$$-\Delta S_m(T)_{\Delta H} = \int [\,\partial M(T,H)\,/\,\partial T\,]_H\, dH$$

The maximum entropy change of 12.8 Kkg^{-1}K^{-1} is obtained at 2 K for $\Delta H = 5$ T. For a system with two Gd^{III} ($S = 7/2$) and seven Cu^{II} ($S = 1/2$) ions which are fully decoupled, the maximum -ΔS_m value of 25.7 Jkg^{-1}K^{-1} can be calculated from the equation -$\Delta S_m = nR\ln(2S+1)$.
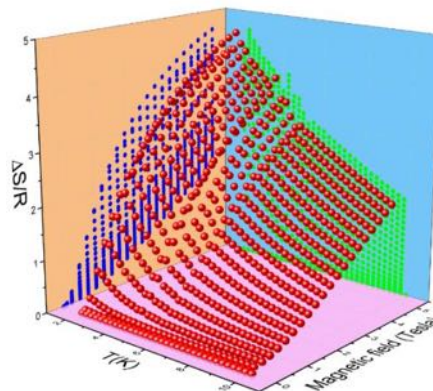

Figure 3. Isothermal magnetization and MCE data for **1**.

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