



Phthalocyanine-based molecular paramagnets. Effect of double-decker structure on magnetothermal properties of gadolinium complexes

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ABSTRACT

Gadolinium is useful in the room temperature magnetic refrigeration due to its large magnetocaloric effect occurring at temperatures close to room. We predict and represent known phthalocyanine complexes as a new class of paramagnets with a large magnetocaloric effect at the temperatures close to room acting due to gadolinium atom located in a coordination site of a conjugated phthalocyanine macrocycle/macrocycles. Magnetothermal properties (a magnetocaloric effect, specific heat capacity, heat released due to MCE, enthalpy/entropy change) of paramagnetic (AcO)GdPc and GdPc²⁻, Pc⁻ phthalocyanine dianion, as the 3% water suspensions at 278–338 K in the magnetic fields of 0–1.0 T were studied for the first time in the family of these paramagnets. The study of magnetothermal properties and specific heat capacity were performed in two independent experiments by microcalorimetry and differential scanning calorimetry, respectively. Large positive MCE in (AcO)GdPc reaches a value of 0.47 K at 278 K when the magnetic field is changed from 0 to 1 T. MCE in GdPc²⁻ is lower by almost an order of magnitude compared with (AcO)GdPc, which indicates that the intramolecular oxidation-activated spin coupling does not prevail over the intermolecular coupling of two radical spins.

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1. Introduction

Both the magnetizing and demagnetizing processes in materials with a large magnetocaloric effect (MCE) was established [1] can be employed for cooling. Magnetic refrigeration is a very promising alternative technology, near room temperature, to conventional gas-compression refrigerators because of its environmentally friendly and highly efficient. The discovery of the quantum nature of single-molecule magnets (SMMs) led to potential applications in quantum computing [2]. At last, a few complexes with specific properties in magnetic feature have been studied as agents for hyperthermia [3].

Depending on the central lanthanide ion, double-decker phthalocyanine complexes, LnPc₂ can show slow magnetization relaxation as SMMs [4,5]. A larger number of coupled magnetic centers rather than individual spins of zero-dimensional complexes are used for increasing the total spin of the molecule in the case of transition metals of the 3d group [6,7]. The spin and orbital atomic

moment in rare earths complexes, conversely, are maximized due to the strong electronic repulsion. The effective energy barrier against magnetic relaxation, U_{ef} of the lanthanide-based SMMs such as the phthalocyanine double-decker family is quantitatively very similar to zero-field energy gap between the two lowest levels Δ [4]. In other words, U_{ef} is determined by the ligand field around a lanthanide ion. For example, the U_{ef} and Δ values observed for [Pc₂Tb]⁻TBA⁺ (TBA is tetrabutylammonium) are equal to 230 cm⁻¹ and 220 cm⁻¹ [8,9]. In addition the effective barrier 230 cm⁻¹ is larger than for any 3d-based SMM to date [4,8].

That's why the temperature ranges in which single-molecule magnet behavior of the double-decker phthalocyanine complexes was observed were far higher than those of the transition-metal-cluster SMMs [8]. The dominant effect of the coordination geometry of the spin carrier on the magnetic properties is indicated for the mixed triple-decker tetrapyrrole complexes of Dy–Dy, Y–Dy, Dy–Y [10] and Dy–Dy [11] in which the intramolecular f–f and antiferromagnetic dipole-dipole interaction respectively are possible. The porphyrin core conformation and hence the ligand field-effect on a lanthanide ion controls the nature and magnitude of spin coupling also in the case when it has another paramagnetic

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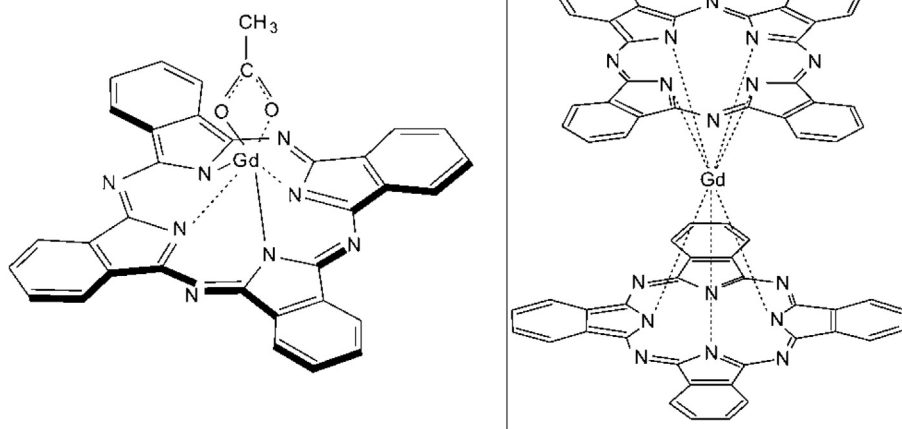


Fig. 1. Structures of (phthalocyaninato) gadolinium(III) acetate, (AcO)GdPc and oxidized (phthalocyaninato) gadolinium(III) double-decker complex, GdPc₂[•].

center, unpaired π -electron in the tetrapyrrole molecule. Temperature-dependent (6–300 K) magnetic susceptibility of [VO(OH₂)(OEP[•])]SbCl₆, (OEP is β -octaethylporphyrin dianion) was characterized from a model in which the vanadyl electron is ferromagnetically coupled to the electron of the porphyrin cation and two radical spins are antiferromagnetically coupled [12]. In this work, J_{V-r} and J_{r-r} parameters which describe the intra- and intermolecular magnetic coupling are equal to 63 cm⁻¹ and -139 cm⁻¹, respectively.

A choosing strategy of our work for deriving a potential molecular system with specific magnetic properties is both a coupling of spin-containing central ion, Gd^{III} with a ferromagnetic coupling unit of an oxidized molecule and a spin density delocalization between Gd^{III} and a readily polarizable aromatic macrocycle. In our recent works [13,14], magnetothermal properties of (porphyrinato) lanthanide(III) acetates/chlorides have been used for measuring a magnetocaloric effect for the first time. Specific heat capacity, the magnetic component of molar heat capacity change, enthalpy/entropy change was in detail observed. The large and giant MCE (porphyrinato) REE complexes displayed a magnetocaloric effect at temperatures close to room were obtained. General strategy of variations in the temperature-dependent magnetic behavior through modification of the porphyrin was provided. It can be assumed that the phthalocyanine analogs of (porphyrinato) REE complexes have the magnetothermal properties useful in the field of room temperature magnetic refrigeration and hyperthermia.

To further correlate magnetic behavior of lanthanide phthalocyanine with a coordination center structure, in particular by to double-decker complex transition, we have undertaken a comparative study of the magnetothermal properties of (phthalocyaninato) gadolinium(III) complexes of 1:1, (AcO)GdPc with axial coordinated acetate and 1:2, GdPc₂[•] oxidized due to one electron removing (Fig. 1).

2. Experimental

2.1. Synthesis of the phthalocyanine complexes

(Phthalocyaninato) gadolinium(III) acetate were prepared from Li₂Pc and Gd(AcO)₃·4H₂O in a molar ratio 1:2.5 in boiling DMSO during 20 min by a literature method [15]. The reaction mixture was cooled and diluted with twice the volume of water. The residue was filtered, washed with water and air-dried. The yield was ca. 90%. Li₂Pc was synthesized from H₂Pc and butyllithium.

UV–vis (DMF): λ_{\max} , nm (logarithm of the molar absorption coefficient, log ϵ) 670 (4.28), 639 (shoulder), 605 (3.39), 338 (3.69). IR (KBr, 350 ÷ 4000)¹: ν , cm⁻¹ 463 (Gd–N), 555 (δ , Pc), 617, 684 (Pc), 735, 741, 766, 1251, 1277 (C–H, Pc), 1555 (deformation vibrations, CH₃), 2853, 2923, 2953 (ν , CH₃), (3014, 3029, 3049, 3057, 3076) (ν , Pc), 874, 884, 1438, 1455 (isoidole ring), 1045, 1060, 1081, 1093, 1118 (combine vibrations, isoidole ring –C–H, Pc), 1112, 1140, 1158, 1185 (Pyr combined with C–H, Pc), 1304, 1320 (Pyr), 1405 (–C=C–N=), 1484 (–N=), 1502, 1591, 1608 (ν , C–C, benzene), 1333 (symmetrical ν , COO, AcO), 1582 (asymmetric ν , COO, AcO). Elemental analysis, calculated for C₃₄H₁₉N₈O₂Gd: C, 56.03; N, 15.37; H, 2.63; and Gd, 21.58%. Found: C, 55.74; N, 15.20; H, 2.74; and Gd, 21.40%.

Oxidized (phthalocyaninato) gadolinium(III) double-decker complex GdPc₂[•] was synthesized using method [16,17] by interaction of 10 g of *o*-phthalonitrile with lanthanide acetate at the temperature of 560 K during 1 h. The product blue-green in color was endured in vacuum at the temperature of 620 K for 1 h. Then one dissolved in DMF (150 ml) with addition of hydrazine hydrate. The solution was filtered and undergone electrolysis with constant current in a cell with graphite cathode and Pt anode. The crystals obtained were filtered, washed with acetone and dried at the temperature of 370 K in air. UV–vis spectrum of GdPc₂[•] in concentrated sulfuric acid have one wide band at λ_{\max} 407 nm, log ϵ = 4.00 in 17.7 M H₂SO₄. UV–vis (CH₂Cl₂): λ_{\max} , nm (relative intensity) 884.0 (0.0869), 668.0 (1), 602.0 (0.232), 459.0 (0.224), 321.0 (0.807). IR (KBr, 350 ÷ 4000): ν , cm⁻¹ 498 (Gd–N), 562 (δ , Pc), 626, 678 (Pc); 727, 740, 778, 1060, 1156, 1174, 1192 1282 (C–H, Pc), 3028, 3048, 3058, 3075 (ν , C–H, Pc), 1113, 1421, 1447, 1463 (isoidole ring), 1319, 1365, 1400 (–C=C–N=), 1483 (–N=), 1500, 1523 (isoidole ring combined with pyrrole ring vibrations), 1509, 1523, 1594, 1607 (ν , C–C, benzene ring). Elemental analysis, calculated for C₆₄H₃₂N₁₆Gd[•]: C, 65.02; N, 18.95; H, 2.73; and Gd 13.30%. Found: C, 64.75; N, 19.08; H, 2.97; and Gd, 13.54%.

The rate constants of complex dissociation in the acid solvents of variable composition (Eq. (1)) was measured spectrophotometrically. The experiment was carried out in a thermostatically controlled glass cell at the temperature of 298 ± 0.1 K.

$$k_{\text{obs}} = 1/\tau \ln[(A_0 - A_{\infty})/(A_{\tau} - A_{\infty})] \quad (1)$$

¹ For IR spectrum in KBr registered on the Avatar 360 FT-IR ESP spectrometer (Fig. 1S), see Online Supplementary Materials.

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