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ACCEPTED MANUSCRIPT 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 reachs 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.

KEYWORDS: gadolinium, (phthalocyaninato) complexes, magnetothermal properties, magnetocaloric effect, heat capacity, molecular structure effect.

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 phtalocyanine 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 $[Pc_2Tb]^{-}TBA^{+}$ (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 3*d*-based SMM to date [4,8].

That's why the temperature ranges in which single-molecule magnet behavior of the doubledecker phthalocyanine complexes was observed were far higher than those of the transition-metalcluster 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

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field-effect on a lanthanide ion controls the nature and magnitude of spin coupling also in the case when it has another paramagnetic 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).



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

2. Experimental

2.1. Synthesis of the phthalocyanine complexes

(Phthalocyaninato) gadolinium(III) acetate were prepared from Li_2Pc and $Gd(AcO)_3 4H_2O$ 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 %. Li_2Pc was synthesized from H_2Pc and butyllitium.

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)*: v, 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 (v, CH₃), (3014, 3029, 3049, 3057, 3076) (v, Pc), 874, 884, 1438, 1455 (isoindole ring), 1045, 1060, 1081, 1093, 1118 (combine vibrations, isoindole 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 (v, C-C, benzene), 1333 (symmetrical v, COO, AcO), 1582 (asymmetric v, 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 hour. The product blue-green in color was endured in vacuum at the temperature of 620 K for 1 hour. 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 $\varepsilon = 4.00$ 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) (Fig. 2S): v, 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 (v, C-H, Pc), 1113, 1421, 1447, 1463 (isoindole ring), 1319, 1365, 1400 (-C=C-N=), 1483 (-N=), 1500, 1523 (isoindole ring combined with pyrrole ring vibrations), 1509, 1523, 1594, 1607 (v, 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.

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

Here A_{τ} , A_0 , A_{∞} is absorbance observed at present time, one when $\tau = 0$, and one when a reaction had terminated, respectively.

2.2. Microcalorimetric experiment

The special calorimetric device, the isothermal-shell microcalorimeter was used for studying magnetocaloric effects of paramagnetic complexes. Its shape and construction are developed and presented in the work [18]. Experiment was performed over the temperature range 278 - 338 K in magnetic fields from 0 to 1.0 T. The measuring microcalorimetric cell with the isothermal shell was placed in the gap of the electromagnet. Switching on the magnetic field causes heating of a ferromagnetic material and the entire contents of the calorimeter cell and the switching off – the cooling. Adiabatic magnetization process was achieved by rapid changes of the magnetic field. The temperature fluctuation in the thermostatically controlled space of the calorimetric cell during the calorimetric experiment was ± 0.0002 °C. The sensitivity of the setup was 2 10^{-5} K. Heat capacity in zero field was measured by means of DSC 204 F1 Phoenix (NETZSCH). The error in MCE and heat capacity measurements was 2%. Every experiment was repeated five times.

Amorphous samples of phthalocyanine complexes synthesized were used for suspensions in which a solid with the average size of particles 25 μ m controlled with polarizing microscope Altami

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

Polar 312 was in the highly disperse state. A solid did not change during microcalorimetric experiment on both size of particles and chemical composition. The spectrophotometric control by means of the Agilent 8453 UV-Visible spectrophotometers of a chemical structure of complexes was used.

2.3. Calculation of the magnetothermal properties parameters

We measured a temperature change in the calorimeter, which occurred as a result of the magnetocaloric effect during the microcalorimetric experiment. Then we introduced a known quantity of Joule heat into the calorimeter. Comparing a temperature rise of the calorimeter as a result of the input of Joule heat and a temperature rise as a result of the MCE, we calculated using the formula (2) the amount of heat QMCE, which was allocated (switching on a magnetic field) as a result of the magnetocaloric effect of particles of a metal complex:

$$Q_{\rm MCE} = Q_{\rm J} \left(\Delta T / \Delta T_{\rm J} \right)$$

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. The amount of heat Q_{MCE} is related to the magnitude of the MCE by ratio (3), which is similar to the fundamental equation of heat balance [19].

(2)

(3)

$$Q_{\rm MCE} = m_{\rm m} C_{\rm P,m} \Delta T_{\rm MCE}$$

Here ΔT_{MCE} – the adiabatic temperature change as result of MCE, Q_{MCE} – heat generated in the calorimetric experiment as a result of MCE when a magnetic field is applied; m_m , $C_{P,m}$ – mass and heat capacity of a magnetic material. Using the experimental values of heat Q_{MCE} , the enthalpy change, $\Delta H_{(enth)}$ of a magnetic material resulting from the changes in the magnetic field may be determined. The values of enthalpy changes of a magnetic material, $\Delta H_{(enth)}$ can be obtained by direct calorimetric measurements. Character of dependences of the change Q_{MCE} and $\Delta H_{(enth)}$ on magnetic induction and temperature are similar to that of the magnetocaloric effect changes, and these values can be used to calculate the cooling capacity of magnetic materials.

Heat capacity in zero fields in solid of complexes was directly measured in experiment in this work. The specific heat capacities of the magnetic particles in the suspensions obtained in [13,14] and used here for comparison were calculated taking into account the assumption of the absence of interaction between components of a heterogeneous system. The heat capacity in such systems is the total of heat capacities of components in accordance with their concentrations. Thus, the specific heat capacity of a solid phase in heterogeneous systems can be calculated from the equations (4) and (5).

$$C_{\rm p(sus)} = C_{\rm p(solid)} \,\omega_{\rm (solid)} + C_{\rm p(water)} \,\omega_{\rm (water)} \tag{4}$$

$$C_{\text{p(solid)}} = (C_{\text{p(sus)}} - C_{\text{p(water)}} \omega_{(\text{water)}}) / \omega_{(\text{solid})}.$$
(5)

Here $C_{p(solid)}$, $C_{p(sus)}$ and $C_{p(water)}$ are specific heat capacities of a solid phase, suspension and water, accordingly, $\omega_{(solid)}$ and $\omega_{(water)}$ are mass fractions of a solid phase and water in a suspension, accordingly. When the values of ΔT , $Q_{MCE} \mu C_{P,m}$ are determined from the experiment, the value of MCE (ΔT_{MCE}) can be calculated (Eq. 2).

The entropy values were calculated from MCE at specified values of C_p and temperature.

2.4. The reliability of the microcalorimetric method

To check the reliability of the developed method, the temperature dependence of MCE of gadolinium was determined. The polycrystalline metallic Gd with chemical purity of 98% was used. De-

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pendences of MCE of the metallic gadolinium on magnetic induction and temperature are well studied. This metal is often used as a reference standard in the study of magnetocaloric properties and cooling performance of magnetic materials [20-22]. Fig. 2 shows temperature dependence of MCE in gadolinium when the magnetic field was changed from 0 to 1.0 T in comparison with the literature data [23,24]. The MCE values were obtained on the basis of equation (2). It is known that the temperature dependence of MCE in Gd due to magnetic phase transition (ferromagnetism – paramagnetism) has a maximum at 292 K. As seen in Fig. 2, experimental values of MCE, obtained by the calorimetric method, are in a good agreement with the literature data.



Fig. 2. Temperature dependence of MCE in gadolinium in magnetic field 0 - 1 T: (1) experimental data from the work [23], (2) our experimental data observed by the microcalorimetric method, (3) experimental data from the work [24], and (4) our experimental data obtained by the microcalorimetric method, based on the heat capacity from the work [25]

To estimate the cooling capacity of highly dispersed magnetic materials, we propose the application of specific heat Q_{MCE}/m (J/kg), which is released or absorbed as a result of MCE with the change of a magnetic field, and which is obtained by direct calorimetric measurements. This value for the metallic Gd is 733 J/kg at 292 K when the magnetic field changes from 0 to 1.0 T.

3. Results and discussion

3.1. Chemical structure and stability in solutions and solid

Chemical structure of (phthalocyaninato) gadolinium(III) acetate is proved due to spectral data and analysis of the elemental composition. UV-vis spectrum of (AcO)GdPc corresponds to the literature data [15] for (phthalocyaninato) lanthanide(III) acetates. Typical UV-vis spectrum of these in organic solvent has long-wave maximum in the region 670 - 700 nm ($\pi \rightarrow \pi^*$ transition [26]) and its oscillation component of lower intensity about 610 nm. Intensive Soret band is disposed at 330- 390 nm. In the lanthanides raw, the UV-vis spectra show low dependence from Ln and acido-ligand nature [14,27,28] but vary markedly wavelength (Table 1). This differs the complexes of 1:1 from double- (Fig. 1) and triple-deckers [15].

Table 1.

Long wave absorption band position in UV-vis spectra of (AcO)GdPc, λ_{max} , nm

Solvent	λ_{max} , nm	Solvent	λ_{max} , nm
DMSO	673.4	Benzonitrile	718.4, 691.2
DMF	670.0	Acetonitrile	663.1
Benzene	677.5	CHCl ₃	675.7
Acetone	666.7	$(C_2H_5)_2O$	670.2
Pyridine	675.7		

Vibrations of the phthalocyanine molecule fragments are reflected in IR spectrum (Experimental, Figs. 1S, 2S). The signals with maximum frequents 1333 and 1582 cm⁻¹ belong to OCO vibrations indicating to bidentate coordination of axial acetate. The difference in the frequency values of valence asymmetric and symmetrical vibration of OCO, 249 cm⁻¹ is a little greater than 225 cm⁻¹ and lower 300 cm^{-1} [29-31] for the ionic complexes and for the monodentate coordination of the carboxyl group, respectively. This relation demonstrates the axial ligand binding by means of weak covalent predominantly ionic bonds Gd-O.

UV-vis spectra of (phthalocyaninato) lanthanide(III) double-decker complexes are mainly identical to those of monophthalocyanines, but there are a small absorption band associated to the semioccupied molecular orbital (SOMO), near 450 nm and an intramolecular charge-transfer band in the 1200–1500 nm range arising due to the radical nature of Ln^{III}Pc₂[•] complexes [32, 33]. A band of low intensity near 890 nm is also observed [32, 34]. GdPc₂ exhibit typical features of the electronic absorption spectra in UV-visible region studied for (phthalocyaninato) rare earth double-decker complexes with the new low-intensity absorptions appearing at 458.0 and 884.0 nm, B band at 321.0 nm and hypsochromically shifted Q band at 668.0 nm.

Transition to double-decker complex noticeable changes a location and a number of C-H bonds, isoindole ring, pyrrole ring and -C=C-N= signals in IR spectrum. The vibrations of phthalocyanine molecule, valence ones of benzene ring C-H and C-C as -N= are practically changeless. The axial ligand signals is absent in IR spectrum. Probably, these peculiarities are determined by not only the chemical structure differences. In addition, distortions of the macrocycle structure take place. Nowadays there is information about structures of $Ce^{IV}(Pc)_2$ [35], NdPc₂ [36], Er^{III}(Pc)₂ [37], and others. Data on sandwich-type complexes the structure of which is studied by X-ray crystallography are listed in [28]. From the results, it is seen that the structure of (phthalocyaninato) doubledecker complexes for all the investigated compounds has the same type. The metal atom is coordinated by eight isoindole nitrogen atoms (N-iso) and is located between two phthalocyanine macrocycles. Macrocycles undergo distortion and become non-planar but saucer-shaped with benzene rings bent outward. The distortion degree as well as M-N-iso distances and rotation of the macrocycles with respect to one another are determined by nature and radius of the metal cation.

Both (AcO)GdPc and GdPc₂[•] are stable in solutions and solid in the absence of acids. GdPc₂[•] do not change in the temperature exposure to 400 K, whereas the first complex undergoes destruction. The complexes are showing significant difference in resistance to acids dissociating slowly in mixed protolytic media namely ethanol - 1.5-3.5 M AcOH and 15.9-17.7 M H₂SO₄ in the case of (AcO)GdPc and GdPc₂, respectively. The first order rate constants of dissociation k^{298K} are equal $(0.61 \pm 0.02) 10^{-3}$ to (AcO)GdPc in ethanol – 4.25 M AcOH and 0.12 10^{-4} s⁻¹ to GdPc₂[•] in 16.9 M H₂SO₄. That is in a good agreement with the earlier results [38, 39]. Amorphous samples of the complexes used for the preparation of water suspensions in magnetocaloric experiment were examined on stability after the stay in the magnetic field through UV-vis spectra.

3.2. Magnetotermal properties

Measurements of DC magnetic susceptibility for bis(octaethyltetraazaporphyrinato) lanthanide(III) under an applied field of 0.1 T [40] shown that the gadolinium(III) complex, unlike terbium(III) and dysprosium(III) analogs with SMM behavior maintains a Curie's constant value in good agreement with that expected for only a spin (S = 7/2) contribution due to absence of spinorbit coupling. Nevertheless gadolinium(III) phthalocyanines display an interesting magnetic behavior at temperatures close to room.

The temperature dependence of the specific heat capacity in zero magnetic field for both (AcO)GdPc and GdPc[•] (Fig. 3) has an extreme character. The effect of magnetic field on the temperature dependence of both complexes practically does not appear and therefore the temperature dependence of specific heat capacity in a magnetic field is not given here.

Fig. 4 represents experimental results for MCE in (AcO)GdPc and GdPc₂[•] in dependence on temperature and magnetic induction. MCE values when magnetic induction starting are positive. MCE value increases with the increasing in the magnitude of magnetic field and non-linearly decrease with temperature growth exhibiting extremes in the studied ranges of temperature and magnetic induction. Character of a changing of MCE is largely determined by the temperature dependence of the specific heat capacity (Fig. 3).



Fig. 3. Temperature dependence of the specific heat capacity (C_p) of (1) (AcO)GdPc and (2) GdPc₂[•] in zero magnetic field

MCE in (AcO)GdPc reaches the value of 0.47 K at B = 1.0 T and T = 278 K (Fig. 4). That in the same complex with porphyrin, (AcO)GdTPP is equal to 1.45 K [14]. The temperature dependence of MCE in (AcO)GdPc has minimum and maximum at 318 K and 338 K, respectively. The values of the MCE in GdPc₂[•] much less than in (AcO)GdPc. The temperature dependence of the MCE in GdPc₂[•] has a peak at 288 K, which increases with increasing magnetic induction.



Fig.4. Temperature dependence of MCE in (a) (AcO)GdPc and (b) $GdPc_2^{\bullet}$ at applied magnetic induction: (1) 1.0, (2) 0.8, (3) 0.6, (4)0.4, and (5) 0.2 T

The temperature dependences of the enthalpy change, $\Delta H_{(enth)}$ and of the entropy change, $\Delta S_{(enth)}$ shown in Figures 5 and 6, respectively have the same character as these of MCE (Fig. 4).

The decrease of MCE values in the series of (AcO)GdTPP, (AcO)GdPc, $GdPc_2^{\bullet}$ allows a qualitative estimate the ratio of contributions of ferromagnetic and antiferromagnetic coupling to magnetic behavior of double-decker complex. Firstly, the entropy changes because of MCE (Fig. 6) are only a few joules per kilogram of paramagnetic material. C_p value in zero magnetic field at the temperature of 288 K in the series mentioned is equal to 1.19, 1.05 and 1.19 J g⁻¹ K⁻¹. The absence of correlation MCE - C_p indicates zero contribution of the effects in lattice subsystem on magnetic behavior of the gadolinium(III) complexes. It means that MCE in ones is connected with the changes in the electronic subsystem. As it was mentioned in Introduction, temperature-depending magnetic

behavior of paramagnets based on 4f metal complexes is connected with slow thermally-activated transition between spin-up and spin-down states. Ligand-field effect depends on both an electronic system of ligands and coordination polyhedron of a central ion. As it was shown on an example of (meso-tetraphenylporphinato) gadolinium(III), thulium(III), and europium(III) chlorides, the macrocyclic ligand in the tetrapyrrole complexes of gadolinium with the stabile $4f^2$ electronic system is bonded without dative π interaction Gd \leftrightarrow N due to σ bonds. There is also an analogy in a coordination center structure of three gadolinium(III) complexes mentioned despite the difference in the coordination numbers in a mono- and bistetrapyrrole complexes. A metal atom in such complexes is displaced from N₄ plane namely of approximately 1.7 [41, 42], 1.26 [43], and 1.450/1.495 [44] Å for (X)Ln^{III}P, (AcO)Lu^{III}Pc, and Gd^{III}H(TPP)(Pc), respectively. The strength of the σ bonding in the isostructural complexes (AcO)GdTPP, (AcO)GdPc grows in the transition to phthalocyanine complex according to data [38, 45-47]. The more strongly is bonded a macrocyclic ligand the better is conditions of the spin carrier - nuclear spins interactions being another important factor of the magnetic behavior of lanthanide phthalocyanines [2]. The negative contribution associated with the growth of the strength of this interaction determines lower MCE in (AcO)GdPc. Besides that, radius of the coordination cavity and the displacement of the Gd atom from its plane in (AcO)GdPc are lower in comparison with porphyrin complex.



Fig.5. Temperature dependence of the enthalpy change, $\Delta H_{\text{(enth)}}$ in (a) (AcO)GdPc and (b) GdPc2[•] at applied magnetic fields: (1) 1.0, (2) 0.8, (3) 0.6, (4)0.4, and (5) 0.2 T



Fig. 6. Temperature dependence of the entropy change, $\Delta S_{(enth)}$ in (a) (AcO)GdPc and (b) GdPc2[•] at applied magnetic fields: (1) 1.0, (2) 0.8, (3) 0.6, (4)0.4, and (5) 0.2 T

In addition to the ligand-field splitting and interactions with nuclear spins, the oxidized π system of one of two macrocyclic ligands having a half-occupied π orbital, SOMO can determine the



magnetic properties $GdPc_2^{\bullet}$. We could expect that the unpaired electron stabilizes the Gd^{III} highspin state due to the promotion of the parallel alignment of the magnetic moments in oxidized (bisphthalocyaninato) complex. Low MCE in GdPc2[•] shows that the antiferromagnetic intermolecular coupling of two radical spins as in [VO(OH₂)(OEP[•])]SbCl₆ [12] which was discussed in Introduction is the predominate contribution to the $GdPc_2^{\bullet}$ spin state. The contribution of the radical centered on the macrocyclic ligand to the overall magnetic moment is also negligible in bis(octaethyltetraazaporphyrinato) gadolinium(III) [40] as well in its terbium and dysprosium analogs. The intramolecular ferromagnetic spin coupling in metall porphyrin π -cation radicals is rationalized as arising from the exchange interaction of unpaired electrons in orthogonal magnetic orbitals [48] in the case of the copper(II) complex with the sterically bulky tetramesitylporphyrin prevented intermolecular aggregation and accompanying porphyrin core ruffling as in CuTPP π -cation radical. The antiferromagnetic coupling in $[CuTPP^{\bullet}]^+$ is rationalized in terms of spin pairing in the bonding molecular orbital in the paper cited.

4 Conclusion

The gadolinium ion of charge 3+ retains its paramagnetic properties being in a porphyrins/phthalocyanines ligand field. As paramagnets, these complexes exhibit a large magnetocaloric effect at temperatures close to room e.g. up to 1.45 and 0.47 K in (AcO)GdTPP and (AcO)GdPc, respectively when the magnetic induction is changed from 0 to 1 T. That is only slightly lower than one in 3*d*-4*f* clusters/homo-metallic gadolinium compounds at higher fields (2.4-3 K at ΔB of 0-7 T) [7]. It could be employed for cooling in home and industrial refrigerators and other devices. Since porphyrins/phthalocyanines and their complexes can selectively accumulate in a tumor of a human body, the tetrapyrrole complexes under consideration promise to expand opportunities of hyperthermia in cancer diagnostics and therapy.

The advantages of lanthanide porphyrins/phthalocyanines over other paramagnets consist firstly in the fact that we can control their magnetothermal properties through structural molecule modification that is unlimited in the chemistry of tetrapyrroles. It was shown above that positive contribution to MCE in gadolinium(III) porphyrine/phthlocyanine give a high spin of the paramagnetic carrier and depending from a macrocycle's electron structure a spin density delocalization between Gd and a macrocyclic system. Negative contributions to a MCE value from both a growing interaction with nuclear spins and the antiferromagnetic intermolecular coupling of two radical spins if there are any. In addition to a written, the paramagnets based on porphyrins/phthalocyanines contain only a small percentage of expensive gadolinium in comparison with the polycrystalline gadolinium. They are soluble in organic media what allows forming from their nanoscaled molecules nanostructures higher order. As the environmentally friendly materials, the complexes studied can replace the toxic compounds used in vapor-compression cycle.

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Phthalocyanine-based Molecular Paramagnets. Effect of double-decker structure on magnetothermal properties of gadolinium complexes

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Fig. 2S. IR spectrum of GdPc₂[•] in KBr

Graphic Abstract

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ACCEPTED MANUSCRIPT Phthalocyanine-based Molecular Paramagnets. Effect of double-decker structure on magnetothermal properties of gadolinium complexes

T.N. Lomova, A.G. Ramazanova, D.V. Korolev, V.V. Korolev, E.G. Mozhzhukhina

Magnetothermal properties of gadolinium(III) single/double-decker phthalocyanine complexes were obtained by microcalorimetry for the first time.

Magnetocaloric effect in (AcO)GdPc reaches the value of 0.47 K at ΔB 0-1 T and T 278 K that is only slightly lower than one in 3*d*-4*f* clusters/homo-metallic gadolinium compounds at higher fields (0-7 T).

The intramolecular oxidation-activated spin coupling does not prevail over the intermolecular coupling of two radical spins in GdPc₂[•].