



# Central atom/substituent effects on magnetothermal properties of metal porphyrins in aqueous suspension



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## ABSTRACT

Magnetothermal properties of (X)Mn<sup>III</sup>P and (X)Ln<sup>III</sup>P, where X = chloro-, bromo-, acetate-ligand; Ln = Eu, Gd, Tm and P = (2,3,7,8,12,13,17,18-octaethylporphyrinato)-, (5,10,15,20-tetraphenylporphyrinato)- or (2,3,7,8,12,13,17,18-octa-*para-tert*-butylphenyltetraazaporphyrinato)-ligand, as 6% water suspensions were determined by the microcalorimetric method at 298–353 K in a magnetic induction of 0–1.0 T. High-disperse complex particles were found to have paramagnetic properties. It was established that positive MCE increases with an increase in magnetic induction at all temperatures and decreases with an increase in temperature at all magnetic inductions; in the case of (Cl)GdTPP actually MCE does not depend on temperature. Dependences of specific heat capacity and that of the change in enthalpy and magnetic entropy of the studied complexes on magnetic induction were explored. The first of these dependencies has a maximum at 0.25–0.35 T at all temperatures. Heat capacity of the lanthanide complexes slightly increases with an increase in temperature; a magnetic component of heat capacity takes place only in (AcO)GdTPP at temperatures above 298 K. The regularities of the influence of central atom, acidoligand and a macrocycle composition in porphyrin complexes on their magnetothermal properties were established. Both a macrocycle composition in the case of manganese complexes and an acidoligand variation in the case of lanthanide complexes are bigger than the other studied factors. We explored prospects for the use of magnetothermal properties in the quantitative determination of thermodynamic characteristics and for revealing trends of changes in the magnetic activity of porphyrin complexes. It was shown that high magnetocaloric effect of (AcO)GdTPP compared with the lanthanum manganite doped by silver ions goes and gets a perspective for a wide range of potential industrial-scale applications in new refrigerating machinery and in a hyperthermia for a medicine.

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## 1. Introduction

Many of the unique properties of porphyrins (H<sub>2</sub>P) and azaporphyrins (H<sub>2</sub>AP) follow from the delocalization of a macrocycle electronic system. This state, combined with high macrocycle stability, leads to participation of the electronic system of macrocycle in the new forms formation when H<sub>2</sub>P/H<sub>2</sub>AP reacts with proton or electron in a solution or in an electrochemical cell. New forms are similar to protonated benzene hydrogen bonded H<sup>+</sup>-associate H<sub>4</sub>P<sup>2+</sup> ··· H<sup>+</sup><sub>solv</sub> obtained in strong concentrated acids [1,2] or π-cation/anion radical [3–6]. H<sub>2</sub>P cations in a solution are of great theoretical and practical interest due to the necessity to elaborate anion receptors. These forms are similar to numerous known cationic porphyrins bonding the anions in solid state

[7–9]. Research on the development of anion receptors based on porphyrins for solutions has begun now [10]. Aza-substituted porphyrins have, in a medium for H<sup>+</sup>-associate H<sub>4</sub>P<sup>2+</sup> ··· H<sup>+</sup><sub>solv</sub> existence, an N-protonated form bonded with one or more protons by means of n-electronic pairs [11]. Cyclic electronic system is involved in this bonding to a sure extent. Radical forms obtained in electrochemical redox reactions of porphyrins, including the porphyrins in the metal complex form (metal porphyrin, MP), are widely investigated as their role in these reactions are large. In our works [12,13], cation radicals have been found to be stable intermediates when studying the stability of porphyrin complexes in the solutions based on aerated sulfuric acid, in reactions of oxidizing the complexes with hydrogen peroxide and in some reactions catalyzed by metal porphyrins.

The existence of the mentioned partially or completely one-electron oxidized-H<sub>2</sub>P/H<sub>2</sub>AP forms shows that the macrocyclic electronic system in them is easily polarized. This is why introduction of metal cation in a porphyrin molecule cavity allows deriving

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chemical compounds having a changeable system of electrons and, in the case of paramagnetic metal cation with localized d or f electrons associated commonly with magnetism, a changeable spin state of the central atom. Delocalization of a charge with metal atom participation is most evidently reflected in a hyper-type electron absorption spectrum (UV–vis). Metals such as manganese and some lanthanides are paramagnets. Coordination of these metal cations with aromatic porphyrin having a changeable system of electrons opens prospects to derive magnetic materials with improved magnetic properties in particular with giant magnetocaloric effect.

The high-spin state of central manganese atom in complexes with cyclic tetrapyrrole ligands is reliably confirmed at measurement of the magnetic susceptibility of their solid samples or solutions. Effective magnetic moment ( $\mu_{\text{eff}}$ ) values are equal to 5.9–6.6, 4.8–5.0 and 3.9  $\mu_{\text{B}}$  for porphyrin complexes of manganese (II), (III) and (IV) correspondingly [14–16]. In the case of  $\mu$ -oxo-dimer [(N<sub>3</sub>)Mn<sup>IV</sup>TPP]<sub>2</sub>O, the antiferromagnetic pairing of the manganese atoms resulted in less  $\mu_{\text{eff}}$  values equal to 1.5–2  $\mu_{\text{B}}$ . Manganese (III) porphyrins are the most stable form among complexes of manganese. They used paramagnetic properties already during elaborating the building blocks of molecular magnets based on manganese porphyrins and their tetraazaanalogs – phthalocyanines [17,18]. Complex macrocyclic core in these materials is a cation in the composition of a charge-transfer complex or a free radical with unpaired electron on the macrocycle. Coordination polymers based on tetra-*meso*-substituted manganese (III) porphyrin tetracyanoethenide [19,20] [Mn<sup>III</sup>P]<sup>+</sup>[TCNE]<sup>-</sup> and oxidized diphthalocyanine InPc<sub>2</sub><sup>•</sup> [21] are examples. Measurements of magnetic susceptibility demonstrate typical Curie–Weiss behavior for polycrystals of the compounds. As it is visible magnetism of the compound of the nonmagnetic element, containing diffuse sp electrons, was induced by oxidized phthalocyanine macrocycle.

In our recent works [22,23], magnetic properties of aromatic macroheterocyclic manganese complexes have been for the first time used for measuring the magnetocaloric effect (MCE), which is well known in magneto chemistry [24], and for receiving the thermodynamic parameters of solid particles of the complex in magnetic induction. Specific heat capacity, enthalpy change, the magnetic component of molar heat capacity change and entropy change were observed in detail. Well-characterized chloro(2,3,7,8,12,13,17,18-octaethylporphyrinato)manganese(III) (Cl)MnOEP was chosen for the purpose [23]. Then, chloro(5,10,15,20-tetraphenylporphyrinato)manganese(III) (Cl)MnTPP and its analogs with bromide and acetate ligands in place of chloride were observed [24]. Influence of manganese (III) complexes' structure modifications on their magnetothermal properties was outlined. General strategy for further determining the influence of molecule structure on MCE value was provided. In order to identify the general relationships between magnetothermal properties and chemical structure of porphyrin complexes, further systematic studies were claimed. Magnetothermal properties of porphyrins were obtained in the above-cited works for the first time.

Paramagnetic lanthanides both in free forms and in chemical compounds are of great interest as well. Past and present interest in the lanthanide porphyrins and phthalocyanines is motivated by their extensive applications in optoelectronics, sorbents chemistry, analysis, and numerous other fields of chemistry. The magnetic properties of rare earth element ions are already used in porphyrins to photosensitize active singlet oxygen formation. These ions can gather in a tumor and be used to accumulate paramagnetic ions that are capable of emitting a signal under the influence of an external magnetic induction in magnetic resonance tomography [25], e.g., a conjugate of 2-(1'-hexyloxyethyl)-2-divinylpyropheophorbide  $\alpha$  with aminophenyl-diethylene-triamine-pentaacetic acid (DTPA) coordinated by gadolinium (III). Such complexes are efficient as

well in diagnostics along with their use in tumor therapy. Introducing additional properties to such remedies, i.e. thermal radiation under influence of a magnetic induction, enhances their diagnostic capability. Porphyrin complexes with ions of rare earth elements (REE) are of particular interest. Studies on introducing magnetic properties into metal porphyrin catalysts to simplify methods deriving solid catalysts and increasing their catalytic activity and recyclability were performed [26]. Paramagnetism of central ions in a frame of polarizable aromatic system in several REE porphyrin complexes has been shown [27] to be a very promising property for achievement a giant MCE.

To explore some of these points, this work is oriented forward to first finding the correlation between magnetothermal properties and a molecular structure of a complex. Chloro(2,3,7,8,12,13,17,18-octaethylporphyrinato)-, chloro(5,10,15,20-tetraphenylporphyrinato)-, bromo(5,10,15,20-tetraphenylporphyrinato)-, (acetato)(5,10,15,20-tetraphenylporphyrinato)- and (acetato)(2,3,7,8,12,13,17,18-octa-*para-tert*-butylphenyltetraazaporphyrinato)manganese (III) **1–5** (Scheme 1) were prepared and their spectral and magnetothermal properties were investigated in detail using electron absorption, IR, <sup>1</sup>H NMR spectroscopy and the microcalorimetric method. Magnetothermal properties of complexes as 6% water suspensions were determined at 298 K in a magnetic induction of 0–1.0 T. The magnetocaloric effect and the heat capacity during the magnetization of highly refined particles of acetato(5,10,15,20-tetraphenylporphyrinato)gadolinium (III), and chloro(5,10,15,20-tetraphenylporphyrinato)europium(III), -gadolinium(III), and -thulium(III) complexes **6–9** (Scheme 1) were determined at the temperatures ranging from 278 to 318 K and magnetic inductions from 0 to 1 T as well. Effects of the macrocycle structure, acidoligand, and metal in the coordination center on magnetothermal properties were examined using the data obtained in this work and preliminary data from other studies [23,24,27]. We showed that modifications of a porphyrin ring offer a better control of magnetothermal properties compared with a change of acidoligands in five-coordinate manganese (III) complexes. On the other hand, variation of the axial ligand is a more important factor for controlling magnetothermal properties than changes in the nature of the lanthanide.

## 2. Experimental

Complexes **1–3** were obtained by the reaction between metal salt and macrocyclic ligand. Complex **4** was synthesized from Compound **2** by the substitution of acidoligand [28].

**Chloro(2,3,7,8,12,13,17,18-octaethylporphyrinato)manganese(III), (Cl)MnOEP, 1.** The complex was synthesized by Adler's method [29] and purified by chromatography on Al<sub>2</sub>O<sub>3</sub> (Brockmann activity grade II). IR (KBr):  $\nu$ , cm<sup>-1</sup> 728, 749, 841, 962, 989, 1019, 1055, 1062, 1112, 1148, 1272, 1315, 1373, 1451, 1464, 1480, 1604, 1632, 2931, 2872, and 2966. UV–vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$ , nm (logarithm of the molarabsorption coefficient, log  $\epsilon$ ) 357 (4.87), 428 (4.17), 473 (4.68), 559 (4.01), 590 (3.76), 687 (3.22), and 787 (3.45). Water suspension of the complex was prepared by dissolving solid complex of measured weight into bidistillate. Mass part of the solid sample was equal to 6%.

**(Acetato)(5,10,15,20-tetraphenylporphyrinato)manganese (III), (AcO)MnTPP, 2.** Synthesis of the complex was performed by the reaction of H<sub>2</sub>TPP with Mn(AcO)<sub>2</sub> in boiling DMFA. The reaction was finished after the disappearance of the porphyrin absorption bands ( $\lambda_{\text{max}}$ , nm (log  $\epsilon$ ) 648 (3.65), 592 (3.75), 551 (3.89), 516 (4.26), 420 (5.43), and 373 (4.37)) in the UV–vis spectrum of the reaction mixture. The complex was extracted by vacuum distillation of DMFA and purified by double chromatography on an alumina column (Brockmann activity grade II) with the use

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