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Mendeleev Commun., 2016, **26**, 301–303

Mendeleev Communications

Phthalocyaninato lanthanide(III) acetates as a new class of molecular paramagnets with large magnetocaloric effect

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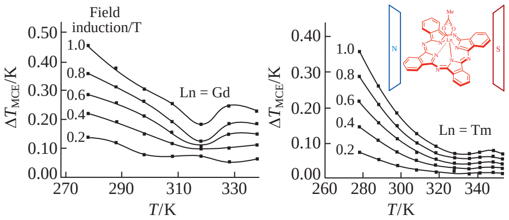
DOI: 10.1016/j.mencom.2016.07.011

Lanthanide(III) ions situated in a coordination site of phthalocyanine macrocycle as molecular paramagnets with a large magnetocaloric effect at the temperatures close to room are presented for the first time on the examples of gadolinium and thulium.



Phthalocyanines form REE complexes with the structure and stoichiometry of several types as the 1 : 1 complexes, (X)LnPc (X is axial anionic ligand), the bisphthalocyaninato double-decker complexes, PcLnPc$^\bullet$ having radical nature, the triple-decker 2 : 3 complexes, PcLnPcLnPc as well as the complexes of the latter type of higher stoichiometry.[1] Sandwich type complexes are used as electrochromic, semiconductive, NLO materials,[2] optically active materials,[3] molecular magnets.[4] The experimental and theoretical study of magnetic properties of the phthalocyaninato/porphyrinato rare earth double- and triple-decker complexes reveals their magnetic field-induced single-molecule magnet nature.[5] The required large moment therein is generated by the unquenched orbital contribution[6] unlike *d*-metal complexes combining the relatively low spin-only moments of several ions into a 'giant spin' ground state by forming nanomagnets.[6,7] Magnetic properties of sandwich-type tetrapyrrole rare earth systems are formed due to a ligand-field splitting, an interaction with nuclear spin and, additionally, a half-occupied π orbital SOMO yielding in an oxidized or reduced complex.[8] Therefore, phthalocyanine complexes with paramagnetic lanthanide ions promise to possess magnetocaloric effect (MCE), when temperature changes in a paramagnetic depend on changing external magnetic field due to redistribution of internal energy of a magnetic substance between the system of magnetic moments of its atoms and crystal lattice in the adiabatic process.

The coordination sphere of the 1 : 1 complexes, (X)LnPc is much less stable than that of the sandwich complexes,[1(*a*),9] therefore, the 1 : 1 complexes are not used in design of materials. However, (X)LnPc attract a great interest as paramagnets with a magnetocaloric effect at temperatures close to 298 K like appropriate porphyrin complexes.[10,11] Namely, MCE of the europium(III), thulium(III), and gadolinium(III) complexes with 5,10,15,20-tetraphenyl-21*H*,23*H*-porphin (H_2TPP) is 0.127–1.45 K, when the magnetic field is changed from 0 to 1.0 T (the 'great magnetocaloric effect'[12]). Our work represents the first success in determination of MCE in REE phthalocyanine complexes of the 1 : 1 type. To further correlate magnetic behavior of lanthanide phthalocyanine with a coordination center structure we carried out the comparative microcalorimetric study of the magnetothermal properties (MCE, a specific heat capacity, a heat released due to MCE, an enthalpy/entropy change) of phthalocyaninato gadolinium(III) and thulium(III) acetates, (AcO)LnPc, as the function of temperature and the magnetic field. In this work we demonstrate that the phthalocyanine complexes, which are more available as compared to the metal porphyrins, dispay practically the same MCE and that their magnetothermal properties can be controlled through modifications in a coordination center structure. We suppose that the studied complexes could be important candidates for new functional molecular materials in magnetic refrigeration near room temperature and in hyperthermia.

The phthalocyaninato lanthanide(III) acetates were obtained by the reaction between metal salt and macrocyclic ligand double-coordinated lithium.[†] Their structure was proved by spectral data and elemental analysis.[‡] UV-VIS spectra of (AcO)GdPc and (AcO)TmPc correspond to the reported data[13] for phthalocyaninato

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[†] (AcO)GdPc and (AcO)TmPc were prepared by reaction of Li_2Pc with $Gd(AcO)_3 \cdot 4H_2O$ and $Tm(AcO)_3 \cdot 4H_2O$, respectively, in a molar ratio of 1 : 2.5 in boiling DMSO for 20 min by a described method.[13] The reaction mixture was cooled and diluted with a double 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 butyllithium.

[‡] *(AcO)GdPc.* UV-VIS [DMF, λ_{max}/nm (logε)]: 670 (4.28), 639 (sh.), 605 (3.39), 338 (3.69). UV-VIS (ethanol, λ_{max}/nm): 670.6, 605, 343. IR (KBr, ν/cm^{-1}): 463 (Gd–N); 555 (out-of-plane) 617, 684 (phthalocyanine); 735, 741, 766, 1251, 1277 (Pc, C–H bonds), 1555 (δ, Me), 2853, 2923, 2953 (ν, Me), 3014, 3029, 3049, 3057, 3076 (ν, Pc); 874, 884, 1405, 1438, 1455 (isoindole ring), 1045, 1060, 1081, 1093, 1118 (combined isoindole ring, Pc C–H bonds); 1112, 1140, 1158, 1185 (pyrrole ring combined with Pc C–H bonds), 1304; 1333 (–C=C–N=); 1484 (–N=); 1502, 1591, 1608 (benzene ring, ν C–C); 1320 (axial ligand, ν_s, COO), 1582 (axial ligand, ν_{as}, COO). Found (%): C, 55.74; N, 15.20; H, 2.74; Gd, 21.40. Calc. for $C_{34}H_{19}N_8O_2Gd$ (%): C, 56.03; N, 15.37; H, 2.63; Gd, 21.58.

(AcO)TmPc. UV-VIS [DMF, λ_{max}/nm (log ε)]: 670 (5.12), 632 (sh.), 605 (4.38), 346 (4.59). IR (KBr, ν/cm^{-1}): 464 (Tm–N); 565 (out-of-plane), 629, 680, 695, 819 (phthalocyanine); 645, 733, 744, 778, 1023, 1162, 1284 (Pc C–H bonds), 1550 (δ, Me), 2854, 2869, 2919, 2959 (ν, Me), 3028, 3050, 3058, 3078 (ν, Pc); 1443 (isoindole ring), 1062, 1081 (combined isoindole ring, Pc C–H bonds); 1115, 1162 (pyrrole ring combined with Pc C–H bonds); 1331 (–C=C–N=); 1487 (–N=); 1487 (benzene ring combined with –N=), 1586, 1606 (ν, C–C); 1455 (axial ligand, ν_s, COO), 1651 (axial ligand, ν_{as}, COO). Found (%): C, 55.07; N, 15.01; H, 2.79; Tm, 22.63. Calc. for $C_{34}H_{19}N_8O_2Tm$ (%): C, 55.15; N, 15.13; H, 2.59; Tm, 22.81.

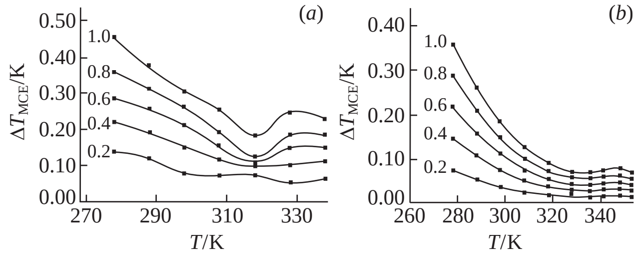

Figure 1 Temperature dependence of ΔT_{MCE} in (*a*) (AcO)GdPc and (*b*) (AcO)TmPc at the indicated field induction (T).

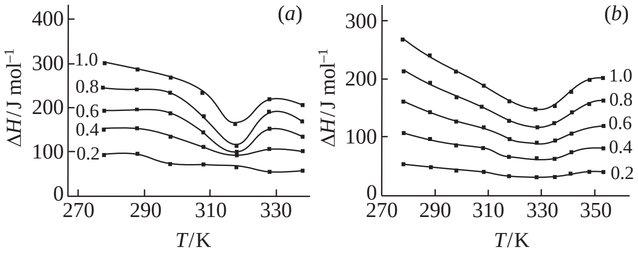

Figure 2 Temperature dependence of the enthalpy change in (*a*) (AcO)GdPc and (*b*) (AcO)TmPc at the indicated field induction (T).

lanthanide(III) acetates. Their typical UV-VIS spectrum in organic solvent has long-wave maximum in the region 670–700 nm ($\pi \rightarrow \pi^*$ transition[14]) and oscillation component of lower intensity at about 610 nm. The intense Soret band is disposed at 330–390 nm. In the lanthanides series, the UV-VIS spectra show low dependence on Ln and axial ligand[11,15] but markedly vary wavelength depending on a solvent.[§] This distinguishes the 1 : 1 complexes (Figure 1) from the double- and triple-decker ones (Table S1).[13]

In the IR spectra,[‡,§] assignment of bands was done according to the data[16] reflecting the vibrations of the phthalocyanine fragments in (AcO)LnPc. The bands with maxima at 1320, 1582 and 1455, 1651 cm^{-1} for gadolinium and thulium complexes, respectively, belong to OCO vibrations in bidentate coordinating acetate.

The complexes studied are stable in both the solutions and the solid state in the absence of an acid and after the magnetocalorimetric experiments. The solid complexes undergo destruction when heated to 400 °C. The complexes show significant difference in resistance to the acids dissociating slowly in mixed protolytic media. That is in good agreement with the earlier results.[15,17]

The magnetothermal properties of (AcO)GdPc and (AcO)TmPc as 3% water suspensions, in which the solid with the average size of the particles 25 μm (polarizing microscope Altami Polar 312) was in the highly disperse state, were studied at 278–338 K in the magnetic field of 0–1.0 T. The suspensions were prepared by the careful mixing of the known portions of the complex taken after synthesis[†] with water directly in the special calorimetric device. The calorimetric cell was placed in the gap of the electromagnet, the isothermal-shell microcalorimeter[18] was used. 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 a calorimetric experiment and the sensitivity of the setup were ±0.0002 and 2×10^{-5} K, respectively, which provides the error in MCE measurements of 2%. To calculate by the equation (1) the heat, which was allocated (switching on a magnetic field) because of the MCE in (AcO)LnPc, we had the temperature changes of calorimetric system due to both the injecting of Joule heat (Q_{J}) and a magnetic field change (ΔT_{J} and ΔT, respectively).

$$Q_{\mathrm{MCE}} = Q_{\mathrm{J}}(\Delta T/\Delta T_{\mathrm{J}}). \tag{1}$$

The MCE values (ΔT_{MCE}) shown in Figure 1[§] were calculated from the Q_{MCE}, mass (m_{m}), and heat capacity ($C_{\mathrm{p,m}}$) values of (AcO)LnPc using equation (2), which is similar to the fundamental heat balance equation.[19]

$$Q_{\mathrm{MCE}} = m_{\mathrm{m}} C_{\mathrm{p,m}} \Delta T_{\mathrm{MCE}}. \tag{2}$$

Using the experimental values of heat Q_{MCE}, the enthalpy change ΔH resulting from the changes in the magnetic field (Figure 2) was determined for (AcO)LnPc.[§] These values characterize the cooling capacity of the paramagnets studied. The temperature dependences of the enthalpy change, ΔH (Figure 2) and the change in entropy, ΔS[§] have the same character as these of MCE (Figure 1).

To check the reliability of the developed method, the temperature dependence of MCE in metallic gadolinium with chemical purity of 98% was determined.[§] The specific heat Q_{MCE} m^{-1} (J kg^{-1}), which is released or absorbed as a result of MCE with the change of a magnetic field, for the metallic Gd is 733 J kg^{-1} at 292 K when the change in the magnetic field is from 0 to 1.0 T.

Figure 1 shows that MCE values on starting the magnetic induction are positive. They non-linearly decrease with temperature rise exhibiting extremes in the studied ranges of temperature and magnetic induction and grow as far as magnetic induction increases.[§] Maximum MCE in (AcO)GdPc and (AcO)TmPc is observed at B = 1.0 T and T = 278 K (0.47 and 0.36 K, respectively) (Figure 1). Character of the MCE change is largely determined by the temperature dependence of the specific heat capacity (Figure 3), for which the general tendency is the increasing in C_{p} value when temperature rises. There are maxima in the graph of the temperature dependence of the specific heat capacity that is more visible in the case of (AcO)GdPc (Figure 3). This could be connected with different thermal changes in the crystal lattice of the complexes. The heating improves the lattice making it uniform and removing voids, *e.g.*, the necessary temperature for improving the crystal structure of erbium(III) bisphthalocyanine is 270 °C.[21] Such variations are especially noticeable in the case of (AcO)TmPc that has a C_{p} value of 1.2 J g^{-1} K^{-1} at 278 K and 3.1 J g^{-1} K^{-1} at 330 K. Effect of a magnetic field on the temperature dependence of both complexes practically is not observed.

Despite the higher values of mass and specific heat capacity [the denominator in the equation (2) for MCE], maximum MCE value in (AcO)TmPc is only 1.3 times less than in (AcO)GdPc [1.6 times in corresponding (Cl)LnTPP[7]]. Paramagnetic moment of Tm^{3+} ion is only slightly lower than that of Gd^{3+} (7.4 and 8.0, respectively[22]). The maximum MCE value in (AcO)GdPc is 3 times less than that in (AcO)GdTPP[11] (0.47 and 1.45, respectively).

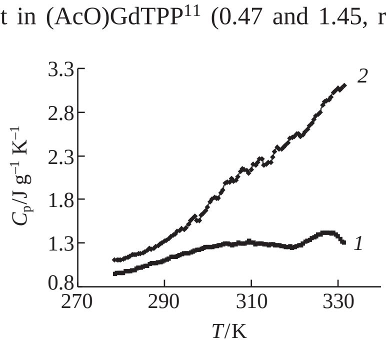

Figure 3 Temperature dependence of the specific heat capacity C_{p} measured in zero field by means of DSC 204 F1 Phoenix (NETZSCH) with error of 2% in (*1*) (AcO)GdPc and (*2*) (OAc)TmPc.

[§] For UV-VIS spectra of (AcO)LnPc in solutions recorded on an Agilent 8453 UV-VIS spectrophotometer (Table S1), IR spectra of (AcO)LnPc in KBr measured on an Avatar 360 FT-IR ESP spectrometer (Figure S1), field dependences of MCE in (AcO)LnPc (Figure S2), field dependences of entropy charge, ΔS, in (AcO)LnPc (Figure S3) and temperature dependence of MCE in gadolinium in comparison with the literature data[20] (Figure S4), see Online Supplementary Materials.

The C_p value also decreases at the transition to phthalocyanine complex.[9] Smaller radius of Tm compared with Gd causes higher planarity and stability of coordination center, which is reflected in a MCE value: the stronger is a macrocyclic ligand bonding the better are conditions of the spin carrier interactions with nuclear spins. That interaction results in decrease in paramagnetic properties. Indeed, the phthalocyaninato gadolinium(III) complex is significantly more stable than its porphyrin analogue and less stable than (AcO)TmPc. The kinetic constants of coordination center dissociation of gadolinium complexes is the same (about 0.6×10^{-3} s^{-1} at 298 K) in ethanol–acetic acid media with AcOH concentration of 4.26 and 0.1 mol dm^{-3} for (AcO)GdPc[23(a)] and (Cl)GdTPP[23(b)] [the data are absent for (AcO)GdTPP], respectively. Complex (AcO)TmPc dissociates with the k_{obs}^{298} of 38×10^{-3} s^{-1} in ethanol–7.44 M AcOH.[23(c)] A relatively slight decrease in (AcO)TmPc MCE mentioned above points out the presence of positive contribution in spin state of thulium-containing paramagnet. That contribution is π-dative interaction Tm→N that starts to notable factor for spin density delocalization in the case of lanthanide complexes with asymmetrically filled *f*-shells.

Finally, the Gd^{3+}/Tm^{3+} ions retain their paramagnetic properties being in a porphyrins/phthalocyanines ligand field. It was mentioned above that a high spin of paramagnetic carrier and depending on electron configuration of one the π dative bonding Ln–N give a positive contribution in MCE. A negative contribution in a MCE value from interaction magnetic moment of spin carrier with nuclear spins depends on strength of the macrocycle bonding. As paramagnets, these complexes exhibit a large MCE (up to 1.45 K when the magnetic induction is changed from 0 to 1 T) at temperatures close to ambient, which could be employed for cooling in home and industrial refrigerators and other devices. For reference, polycrystalline gadolinium and gadolinium ferrite, $GdFeO_3FeO$, display MCE of 2.56 K (at 293 K and field change from 0 to 1.0 T) and 0.42 K (at 298 K, 0–0.65 T), respectively.[24] As the environmentally friendly paramagnets, the complexes of this class can replace the toxic compounds used in a vapor-compression cycle. The gadolinium porphyrins/phthalocyanines contain only a small percentage of expensive gadolinium in comparison with the polycrystalline Gd. They are soluble in organic media, which allows the nanostructures of higher order to be formed. Since porphyrins/phthalocyanines and their complexes can selectively accumulate in a tumor of a living organism, the tetrapyrrole complexes under consideration promise to expand opportunities of hyperthermia in cancer diagnostics and therapy. However, it is firstly important in terms of the advantages of lanthanide porphyrins/phthalocyanines over other paramagnets that we can control their magnetothermal properties through modifications in a molecule structure.

This work (synthesis and control of the chemical structure of the complex) was supported by the Russian Foundation for Basic Research (grant no. 15-03-00646-a) and was carried out with the help of the Centre of the Scientific Equipment Collective Use 'The Upper Volga Region Centre of Physicochemical Research'.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.07.011.

References

1 (*a*) T. N. Sokolova, T. N. Lomova, V. V. Morozov and B. D. Berezin, *Russ. J. Coord. Chem.*, 1994, **20**, 603 (*Koord. Khim.*, 1994, **20**, 637); (*b*) H. Shang, H. Wang, K. Wang, J. Kan, W. Cao and J. Jiang, *Dalton Trans.*, 2013, **42**, 1109; (*c*) V. V. Kalashnikov, V. E. Pushkarev and L. G. Tomilova, *Russ. Chem. Rev.*, 2014, **83**, 657; (*d*) J. Jiang and D. K. P. Ng, *Acc. Chem. Res.*, 2009, **42**, 79; (*e*) A. G. Martynov, Yu. G. Gorbunova and A. Yu. Tsivadze, *Russ. J. Inorg. Chem.*, 2014, **59**, 1635.

2 (*a*) H. Isago, *J. Porphyrins Phthalocyanines*, 2014, **18**, 762; (*b*) A. Hassan, T. Basova, A. G. Gürek and V. Ahsen, *J. Porphyrins Phthalocyanines*, 2013, **17**, 454; (*c*) M. M. Ayhan, A. Singh, C. Hirel, A. G. Gürek, V. Ahsen, E. Jenneau, I. Ledoux-Rak, J. Zyss, C. Andraud and Y. Bretonnière, *J. Am. Chem. Soc.*, 2012, **134**, 3655.

3 W. Lv, P. Zhu, Y. Bian, C. Ma, X. Zhang and J. Jiang, *Inorg. Chem.*, 2010, **49**, 6628.

4 (*a*) N. Giménez-Agulló, C. Sáenz de Pipaón, L. Adriaenssens, M. Filibian, M. Martínez-Belmonte, E. C. Escudero-Adán, P. Carretta, P. Ballester and J. R. Galán-Mascarós, *Chem. Eur. J.*, 2014, **20**, 12817; (*b*) N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara and Y. Kaizu, *J. Am. Chem. Soc.*, 2003, **125**, 8694; (*c*) T. Fukuda, N. Shigeyoshi, T. Yamamura and N. Ishikawa, *Inorg. Chem.*, 2014, **53**, 9080.

5 K. Wang, S. Zenk, H. Wang, J. Dou and J. Jiang, *Inorg. Chem. Front.*, 2014, **1**, 167.

6 N. Magnani, *Int. J. Quantum Chem.*, 2014, **114**, 755.

7 J. W. Sharples and D. Collison, *Polyhedron*, 2013, **66**, 15.

8 N. Ishikawa, M. Sugita and W. Wernsdorfer, *Angew. Chem. Int. Ed.*, 2005, **44**, 2931.

9 T. N. Lomova and M. E. Klyueva, in *Encyclopedia of Nanoscience and Nanotechnology*, ed. H. S. Nalwa, American Scientific Publishers, Valencia, CA, 2004, vol. 2, pp. 565–585.

10 V. V. Korolev, D. V. Korolev, T. N. Lomova, E. G. Mozhzhukhina and A. G. Zakharov, *Russ. J. Phys. Chem. A*, 2012, **86**, 504 (*Zh. Fiz. Khim.*, 2012, **86**, 578).

11 T. N. Lomova, V. V. Korolev and A. G. Zakharov, *Mater. Sci. Eng. B*, 2014, **186**, 54.

12 (*a*) V. K. Pecharsky and K. A. Gschneidner, Jr., *Phys. Rev. Lett.*, 1997, **78**, 4494; (*b*) A. Fujita, S. Fujieda, Y. Hasegava and K. Fukamichi, *Phys. Rev. B*, 2003, **67**, 104416; (*c*) E. Z. Valiev, I. F. Berger, V. I. Voronin, V. A. Glazkov, A. A. Kaloyan and K. M. Podurets, *Phys. Solid State*, 2014, **56**, 14.

13 N. B. Subbotin, L. G. Tomilova, N. A. Kostromina and E. A. Luk'yanetz, *Zh. Obshch. Khim.*, 1986, **56**, 397 (in Russian).

14 V. A. Kuz'mitskii, K. N. Solov'ev and M. P. Zvirko, in *Porfiriny: spektroskopiya, elektrokhimiya, priminenie (Porphyrins: Spectroscopy, Electrochemistry and Application)*, ed. N. S. Enikolopyan, Nauka, Moscow, 1987, pp. 7–27 (in Russian).

15 T. N. Lomova and L. G. Andrianova, *Russ. J. Coord. Chem.*, 2004, **30**, 660 (*Koord. Khim.*, 2004, **30**, 700).

16 (*a*) M. Cheremisina, *Russ. J. Struct. Chem.*, 1978, **19**, 286 (*Zh. Strukt. Khim.*, 1978, **19**, 336); (*b*) T. N. Lomova and B. D. Berezin, *Russ. J. Coord. Chem.*, 2001, **27**, 85 (*Koord. Khim.*, 2001, **27**, 96); (*c*) F. A. Kolokolov, N. N. Bukov and V. T. Panyushkin, *Russ. J. Gen. Chem.*, 2003, **73**, 1942 (*Zh. Obshch. Khim.*, 2003, **73**, 2053); (*d*) A. V. Ziminov, S. M. Ramsh, I. G. Spiridonov, T. A. Yurre, T. G. Butkhuzi and A. M. Turiev, *Vestnik Sankt-Peterburgskogo Universiteta, Ser. 4*, 2009, **4**, 95 (in Russian); (*e*) R. Aroca, D. Battisti, E. A. Lukyanetz and L. G. Tomilova, *J. Mol. Liquids*, 1992, **53**, 147; (*f*) F. Lu, Q. Yang, J. Cui and X. Yan, *Spectrochim. Acta, Part A*, 2006, **65**, 221.

17 T. N. Lomova and L. G. Andrianova, *Russ. J. Phys. Chem. A*, 2000, **74**, 1432 (*Zh. Fiz. Khim.*, 2000, **74**, 1587).

18 V. V. Korolev, A. S. Romanov and I. M. Aref'ev, *Russ. J. Phys. Chem.*, 2006, **80**, 464 (*Zh. Fiz. Khim.*, 2006, **80**, 548).

19 M. M. Popov, *Termometriya i kalorimetriya (Thermometry and Calorimetry)*, Izd. MGU, Moscow, 1954, p. 943 (in Russian).

20 (*a*) A. S. Andreenko, K. P. Belov and S. A. Nikitin, *Sov. Physics Uspekhi*, 1989, **32**, 649 (*Usp. Fiz. Nauk*, 1989, **158**, 553); (*b*) O. V. Melnikov, *PhD Thesis*, MGU, Moscow, 2008, p. 23; (*c*) D. S. Simons and M. B. Salamon, *Phys. Rev. B*, 1974, **10**, 4680.

21 A. G. Gürek, T. Basova, D. Luneau, C. Lebrun, E. Kol'tsov, A. K. Hassan and V. Ahsen, *Inorg. Chem.*, 2006, **45**, 1667.

22 F. A. Cotton, G. Wilkinson and P. L. Gaus, *Basic Inorganic Chemistry*, 3rd edn., Wiley, New York, 1995.

23 (*a*) B. D. Berezin and T. N. Lomova, *Reaktsii dissotsiatsii kompleksnykh soedinenii (Dissociation Reactions of Complexes)*, Nauka, Moscow, 2007 (in Russian); (*b*) L. G. Andrianova, T. N. Lomova and B. D. Berezin, *Koord. Khim.*, 1988, **14**, 459 (in Russian); (*c*) T. N. Lomova and L. G. Andrianova, *Zh. Neorg. Khim.*, 1994, **39**, 2011 (in Russian).

24 (*a*) A. M. Tishin and Y. I. Spichkin, *The Magnetocaloric Effect and Its Applications*, IoP Publishing, Bristol, 2003; (*b*) D. V. Korolev, V. V. Korolev, T. N. Lomova, E. G. Mozhzhukhina and A. G. Zakharov, in *V Regional Conference of Young Scientists 'Theoretical and Experimental Chemistry of Liquid-phase Systems' (Krestovsky Reading)*, Ivanovo, 2010, p. 28 (in Russian).

Received: 22nd January 2016; Com. 16/4824