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Influence of Polymorphism on the Magnetic Properties of Single-Molecule Magnets According to the Data of EPR Spectroscopy in the Terahertz Range

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Abstract—Two earlier described polymorphous modifications of the cobalt(II) (pseudo)clathrochelate are studied by EPR spectroscopy in the terahertz range, where the complex exhibits the properties of a single-molecule magnet (including the record-breaking barrier for magnetization reversal at the moment). Different values of the magnetization reversal barrier found previously for the corresponding crystalline phases by the results of magnetometric measurements in an alternating magnetic field are observed in the EPR spectra in the terahertz range. A combined analysis of these two methods allows one to more precisely estimate the magnetization reversal barrier for two polymorphous modifications and also the contribution of different magnetic relaxation mechanisms to the spin dynamics. This unambiguously confirms that slight changes in the crystalline environment of the molecule of even such structurally rigid metal complexes as cobalt(II) (pseudo)clathrochelates can result in high differences in the magnetization reversal barrier, which is the key characteristic of single-molecule magnets.

Keywords: clathrochelates, cobalt complexes, single-molecule magnets, magnetometry in alternating magnetic field, EPR spectroscopy in terahertz range

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INTRODUCTION

The studies of single-molecule magnets (SMM), viz., chemical compounds capable of manifesting the properties of macroscopic magnets already at the level of an individual molecule, become popular in the world scientific society in the recent time [1]. This makes it possible to produce from them devices of superdense information storage [2] and molecular spintronics [3] and to use them as quantum bits (qubits) for quantum computers [4]. One of the main characteristics of SMM is slow magnetic relaxation, which is primarily caused by their very high magnetic anisotropy [5]. In the case of complexes of the first row transition metals, this phenomenon is related to the splitting energy in the zero field (D) of the metal ion [6], which results in the appearance of the barrier (often named the Orbach barrier) for the thermally activated process of magnetization reversal [7]. However, the properties of SMM are determined not only by the magnetization reversal barrier (MRB) but also by other magnetic relaxation mechanisms, whose contribution to the spin dynamics of the system depends on the nature and structure of the compound under study, its phase state, intermolecular interactions, and even temperature and external magnetic field [8].

We have recently shown [9] that a minor change in the molecular structure of the complex caused by differences in the conformation of the substituent at the periphery results in drastic changes in the MRB. A similar manifestation of conformational polymorphism was found for the cobalt(II) (pseudo)clathrochelate, which is one of the representatives of the unique class of structurally rigid complexes [10], where the metal ion is reliable shielded from the influence of external factors by the cage ligand. This imparts high thermal and chemical stability to the complexes and also provides wide possibilities of their chemical modification (at two apical and four edge positions of the ligand) due to which the cobalt(II) (pseudo)clathrochelates have been considered up to the recent time [9] as ideal candidates to the role of SMM, whose properties can be controlled by the molecular design methods [9, 11–13].

However, magnetometry in an alternating magnetic field, which is actively used for the evaluation of the MRB of the metal complexes [14], does not directly measure this characteristic but gives only an approximate value from the modeling of the temperature dependence of the magnetization relaxation time using the function with many unknowns [15], only one

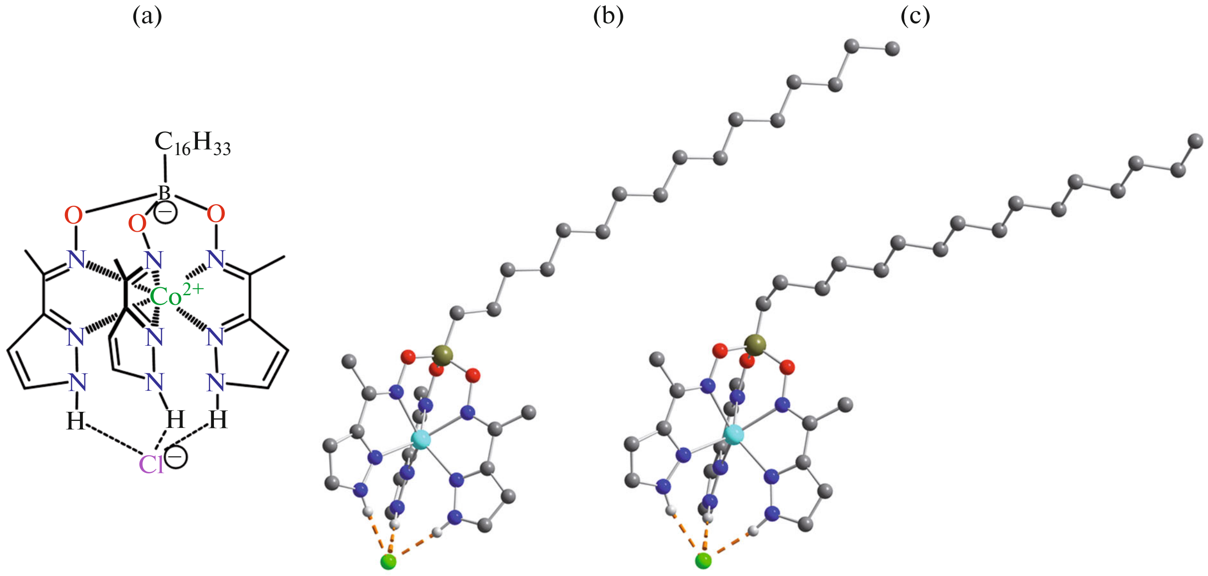

Fig. 1. (a) Scheme of complex **I** and its general view in the crystals of (b) α-**I** and (c) β-**I** according to the X-ray diffraction data [9].

of which being the Orbach MRB. The result of this analysis often does not reflect the real structure of energy levels of the compound under study but is one of many existing sets of parameters corresponding to the obtained experimental data.

The solution of this problem is the application of EPR spectroscopy in the terahertz range for these purposes. However, this method is available only in several scientific institutions in the world. The method makes it possible to detect transitions between various electronic levels in a wide energy range (to several hundreds cm^{-1}) [16] and to determine thus the MRB of the studied compound by the difference in energies between the Kramer doublets [17].

In this work, two earlier synthesized polymorphous modifications of cobalt(II) (pseudo)clathrochelate α-**I** and β-**I** (Fig. 1) in which the clathrochelate exhibited the properties of the SMM with different values of the MRB [9] were studied using EPR spectroscopy in the terahertz range. In combination with the data of magnetometry in permanent and alternating magnetic fields this method made it possible to estimate the barriers more precisely, as well as the contributions of different magnetic relaxation mechanisms to the spin dynamics of two crystalline phases.

EXPERIMENTAL

EPR spectroscopy. EPR spectra in the terahertz range (THz-EPR) were recorded according to a described procedure [18–20] on the terahertz (THz) line of a BESSY II synchrotron (Berlin, Germany) for the same crystalline samples of the cobalt(II) (pseudo)clathrochelates for which the magnetometric measurements in permanent and alternating magnetic fields have previously been carried out [9] without the subsequent purification from eucosane used for preventing crystallite orientation in the magnetic field. An arc mercury lamp was used as a light source in an IFS 125 IR spectrometer (Bruker). The resolution was 1 cm^{-1}, and the acquisition number at each value of the external magnetic field was not lower than 768. A silicon bolometer with liquid helium cooling (Infrared Laboratories) served as a detector. The MRB was calculated in terms of the zero-field splitting formalism from the difference in energies between the Kramer doublets. In particular, for the high-spin cobalt(II) ion ($S = 3/2$) the energy of the second Kramer doublet is equal to the MRB.

Combined analysis of the data of EPR spectroscopy in the terahertz range and magnetometry in permanent and alternating magnetic fields. The magnetometry data (including the temperature dependence of the magnetic susceptibility and field dependence of the magnetization) obtained earlier for polymorphs α-**I** and β-**I** [9] were simulated taking into account the MRB measured by EPR spectroscopy in the terahertz range using spin-Hamiltonian (1) in the PHI program [21]

$$\hat{\mathscr{H}} = \frac{D}{\hbar}\left(S_z^2 - \frac{S^2}{3}\right) + \frac{\mu_\beta}{\hbar} gB\hat{S}, \tag{1}$$

where $\hbar$ is Planck's constant, μ_β is the Bohr magneton, g is the electronic g tensor, B is the induction of the external magnetic field, $\hat{S}$ is the electron spin operator, D is the splitting energy in the zero field, and $U = 2|D|$, where U is the MRB determined from the THz-EPR spectra.

To determine the contributions of various mechanisms to the magnetization relaxation, the data of magnetometry in an alternating magnetic field for polymorphs α-**I** and β-**I** [9] were modeled using Eq. (2)

$$\tau^{-1} = B + CT^n + \tau_0^{-1}\exp(-U/kT), \qquad (2)$$

where A, C, and n are coefficients, τ_0 is the time constant, k is the Boltzmann constant, T is temperature, and U is the MRB determined from the THz-EPR spectra.

RESULTS AND DISCUSSION

The crystalline samples, which were synthesized and characterized in detail earlier [9], were used for the detection of the THz-EPR spectra for polymorphs α-**I** and β-**I** (Fig. 1). This allowed us to study the same crystalline phases, since the required polymorphous modification cannot always be prepared even under the same crystallization conditions [22], and also to carry out a combined analysis by THz-EPR spectroscopy and magnetometry in permanent and alternating fields.

In both cases, the THz-EPR spectra contained (Figs. 2a, 3a) many lines the most part of which were of the vibrational nature. We are interested in detecting signals of the magnetic dipole nature corresponding to the MRB for the high-spin cobalt(II) ion (S = 3/2). To detect these signals, we used the standard approach, the essence of which is the division of the recorded THz-EPR spectra at the chosen values of the magnetic field into the THz-EPR spectra detected at other values of the magnetic field (Figs. 2b, 3b). This allowed us to unambiguously reveal the signals at 230 and 170 cm^{-1} for polymorphs α-**I** and β-**I**, respectively, and thus to directly measure their MRB (230 cm^{-1} for α-**I** and 170 cm^{-1} for β-**I**). They correspond to the splitting energies in the zero field D, being –115 and –85 cm^{-1} ($U = 2|D|$, where U is MRB). Note that fairly close values of D (–111 and –74 cm^{-1}) but with a lower reliability were earlier obtained from an analysis of the magnetometric data in an alternating magnetic field [1]. Although the sign of the splitting energy in the zero field cannot be determined using either THz-EPR spectroscopy, or magnetometry, it is no doubt for polymorphs α-**I** and β-**I** that the sign is negative because of the very high MRB and observed magnetization hysteresis [9].

The obtained values of D (–115 and –85 cm^{-1} for polymorphs α-**I** and β-**I**, respectively) were then used for the modeling of the temperature dependence of the magnetic susceptibility (Fig. 4) and the dependence of the magnetization on the applied magnetic field (Fig. 5), which were earlier obtained for the same crystalline samples [9]. The modeling was performed using spin-Hamiltonian (1) and gave exacter values of g tensor for two polymorphs: $g_\perp$ = 2.40 and $g_{||}$ = 2.69 for α-**I** and $g_\perp$ = 2.16, $g_{||}$ = 2.50 for β-**I**. It is important that an excellent coincidence of the calculated and experimental data with the splitting energies in the zero field calculated from the THz-EPR spectra was achieved even in the case of the axial symmetric g tensor, whereas a satisfactory convergence was earlier observed [1] only when the orthorhombic g tensors {2.50, 2.20, 2.69} and {2.12, 2.00, 2.52} were used for polymorphs α-**I** and β-**I**, respectively.

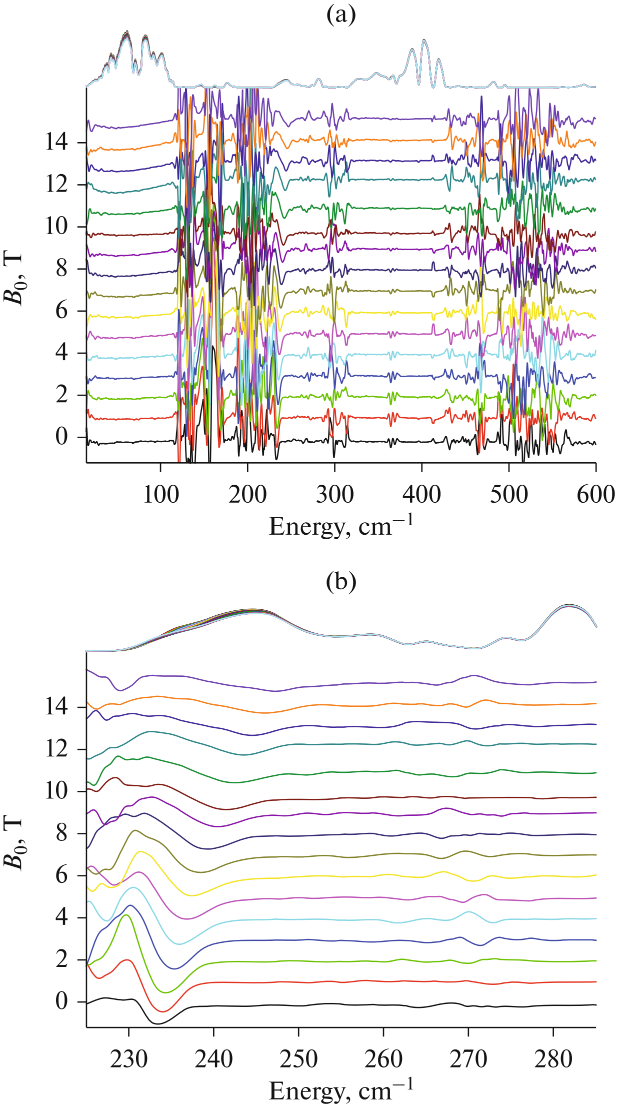

Fig. 2. (a) Differential THz-EPR spectra for α-**I** obtained by the division of the spectrum in the field B_0 + 2T into the spectrum at B_0 and (b) the spectral range 220–290 cm^{-1} containing the signal, whose position depends on the external field.

According to the results of the analysis combining THz-EPR and magnetometry, both polymorphs are the true SMM, since they demonstrate the slow magnetization relaxation in the zero external magnetic field (Fig. 6). The temperature dependence of the

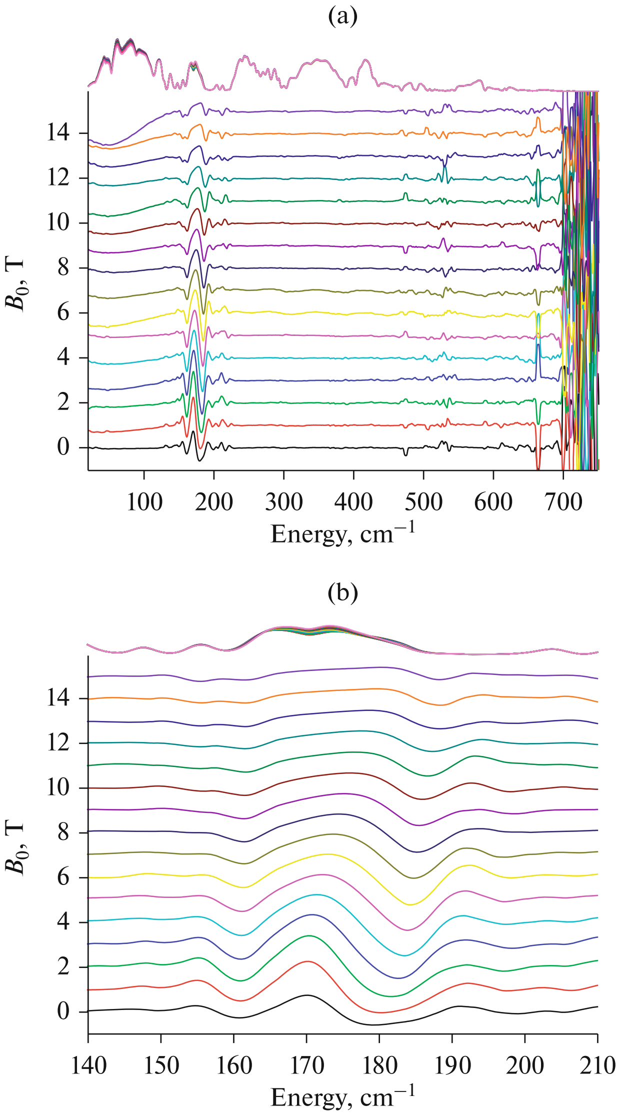

Fig. 3. (a) Differential THz-EPR spectra for β-**I** obtained by the division of the spectrum in the field B_0 + 2T into the spectrum at B_0 and (b) the spectral range 140–210 cm^{-1} containing the signal, whose position depends on the external field.

magnetization relaxation time τ in the coordinates ln(τ)–T^{-1} deviates from linearity, indicating the existence of side mechanisms of magnetic relaxation. The modeling of the magnetometry data in an alternating magnetic field obtained previously for polymorphs α-**I** and β-**I** [9] by Eq. (2) made it possible to determine the relative contributions of all indicated mechanisms to their spin dynamics (Fig. 6). When data of THz-EPR spectroscopy are inavailable, a similar analysis results in a substantial underestimation of the MRB, which was 180.2 and 109.4 cm^{-1} instead of 230 and 170 cm^{-1} for α-**I** and β-**I**, respectively, and in incorrect values of the parameters for other magnetic relaxation mechanisms.

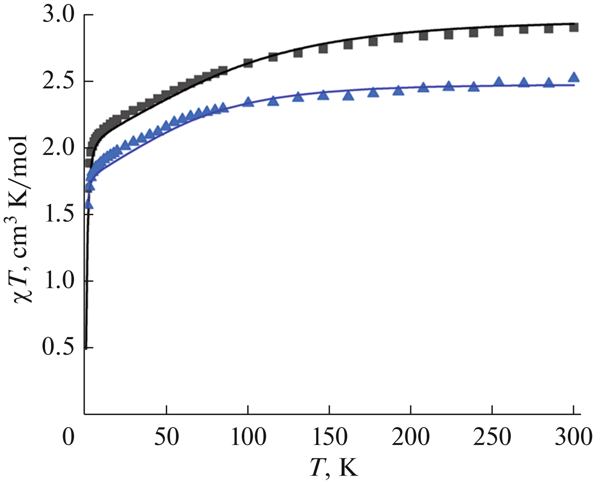

Fig. 4. Temperature dependences of the magnetic susceptibility for (squares) α-**I** and (triangles) β-**I**. Solid lines show the results of data modeling.

In the case of polymorph α-**I**, using the values of MRB determined from the THz-EPR data we succeeded to approach the temperature dependence of the magnetization relaxation time without the contribution of quantum tunneling (zero value of the *B* parameter in Eq. (2)). This explains why the magnetization hysteresis is retained below 4 K for polymorph α-**I** , whereas for β-**I** the magnetization hysteresis is hardly noticeable even at 2 K [1], since a lower symmetry of the cobalt(II) ion environment in the second polymorph results in the activation of the quantum tunneling of magnetization as an alternative temperature-independent mechanism of magnetic relaxation. This fact additionally confirms that new SMM with a decreased probability of the quantum tunneling of magnetization as a side mechanism can be designed on the basis of transition metal clathrochelates. This side mechanism is the main reason for a decrease in the observed MRB due to the control of the symmetry of the coordination polyhedron of the metal ion [23].

Using EPR spectroscopy in the terahertz range combined with the data of magnetometry in permanent and alternating magnetic fields, we estimated with a high accuracy the MRB for two polymorphous modifications of the cobalt(II) (pseudo)clathrochelate in which the properties of an SMM were manifested to different extents [9], and the contributions of different mechanisms of magnetic relaxation to the spin dynamics were also evaluated. The chosen complex, as well as other metal (pseudo)clathrochelates, differs from other complexes by the "conservative" molecular geometry [11] in which the metal ion is almost completely isolated from the influence of the

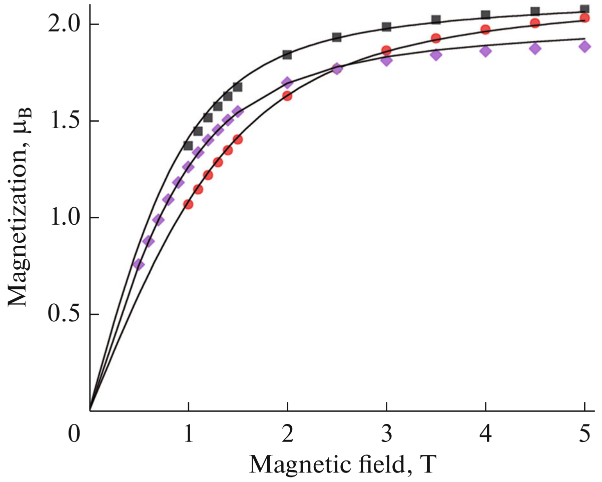

Fig. 5. Magnetization vs. applied magnetic field for α-**I** at (squares) 2 K and (circles) 3 K and (rhombuses) for β-**I** at 2 K. Solid lines show the results of data modeling.

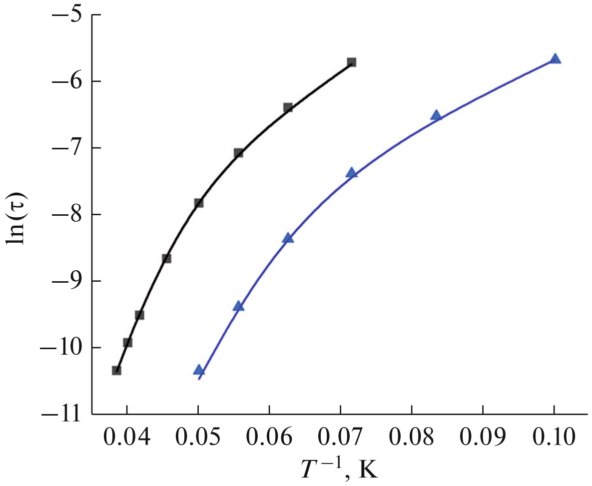

Fig. 6. Temperature dependences of the magnetization relaxation time in the zero permanent magnetic field for (squares) α-**I** and (triangles) β-**I**. Solid lines show the results of data modeling. The R^2 factor is 0.999 for α-**I** and 0.998 for β-**I**. The determined parameters are as follows: $B = 0$, $C = 5.90 \times 10^{-4}$ s^{-1} K^{-5}, $\tau_0 = 1.21 \times 10^{-10}$ s, $n = 5$, and $U =$ 230 cm^{-1} (α-**I**); $B = 23.0$ s^{-1}, $C = 2.74 \times 10^{-3}$ s^{-1} K^{-5}, $\tau_0 =$ 1.84×10^{-10} s, $n = 5$, and $U = 170$ cm^{-1} (β-**I**).

environment by the rigid cage ligand [10]. The latter is basically important for control of the properties of the SMM using the molecular design method [24]. However, even in this case, slight changes in the crystalline environment of the molecule, which cannot be predicted, can induce high distinctions in the MRB, thus noticeably complicating the search for efficient SMM for practical applications in devices of superdense information storage and ultrafast data processing.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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