

## Magnetic Properties of a New Er(III) Macrobicyclic Complex Studied by EPR

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**Abstract.** The macrobicyclic ligands of a Schiff base form complexes with various lanthanide metal cations, where the lanthanide ion can be coordinated in the mono- or binuclear systems. As a result of the Schiff-base condensation, a new erbium cryptate complex has been synthesized and investigated by electron paramagnetic resonance EPR technique. The measurements in the 3.9–300 K temperature range confirmed the presence of the 1:1 macrobicyclic Schiff base–Er<sup>3+</sup> complex. Computer simulations of the registered EPR spectra have revealed the existence of low-symmetry crystal field at the Er(III) site. The complicated EPR spectra of Er(III) complex with an effective spin  $S = 1/2$  in low magnetic fields (<200 mT) were observed only below 60 K. At 5 K the anisotropic  $g$ -factors and the integrated intensity reached local maximum values. In the 5–13 K temperature range the line width and  $g$ -factors remained constant, while the integrated intensity strongly decreased with increasing temperature. Above 13 K a strong increase of  $g_r$ -factor and  $\Delta B_r$  line width was observed. The observed peak in integrated intensity indicates that the EPR signal is produced by the excited state that lies 6.3 K above the nonmagnetic ground state.

### 1 Introduction

The magnetic properties of trivalent rare-earth ions and their complexes with organic materials attract much attention in various research areas. They are widely used in biology and medicine as spectroscopic and magnetic probes and find numerous applications in optoelectronics as photoluminescence materials [1]. The most promising property of erbium with organic materials is the possibility of excitation of a narrow temperature-independent luminescence. Erbium is chosen because the  ${}^4I_{13,2} \rightarrow {}^4I_{15,2}$  transition involving the 4f core electrons of an Er<sup>3+</sup> (4f<sup>11</sup>) ion occurs at the wavelength of 1.54  $\mu\text{m}$ , where an absorption minimum in silica-based optical fibers is observed [2]. Because of this photoluminescence, there are many papers reporting erbium complexes in silica-based optical fibers. Weak electron paramagnetic resonance (EPR) signal from the Er<sup>3+</sup> ions was observed at a cubic-symmetry site under the near band-gap illumination and at a monoclinic site without illumination in an oxygen-coimplanted sample [3]. Organic ligands,

e.g., Schiff bases, form an interesting group of compounds characterized by high affinity to rare-earth cations [4]. Their complexes have been often used for extraction of metal cations, molecular recognition and various types of catalytic reactions [5–7]. Recently, we investigated the spectroscopic and magnetic properties of the complex of macrobicyclic Schiff base (MSB) and  $Gd^{3+}$  metal cation in which the monometallic substitution of the lanthanide ion in the macrobicyclic ligand cavity was detected [8]. Nevertheless, so far, there are only a few reports on the EPR spectra and spin Hamiltonian parameters of MSB ligand with erbium.

In this paper we report a detailed variable-temperature EPR study on the crystalline-powder erbium complex with the Schiff base ligand. The information on magnetic properties of this complex will be extracted from the obtained temperature variations of all available EPR parameters.

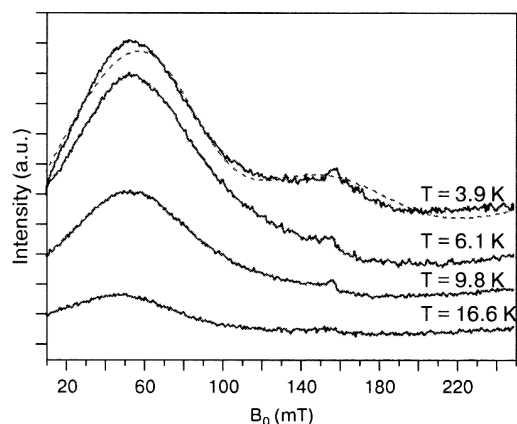
## 2 Material and Methods

The synthesis of the MSB- $Er^{3+}$  complex has been carried out according to a known method described by Platas et al. [9]. Tris-(2-aminoethyl)amine (tren) was added to a solution of erbium(III) nitrate pentahydrate ( $Er(NO_3)_3 \cdot 5H_2O$ ) in hot methanol and refluxed for 10 min. Then 2-hydroxy-5-methyl-1,3-benzenedicarboxaldehyde in methanol was added to this solution and refluxed for 30 min. A yellow solid precipitated upon cooling for 12 h. The crystalline powder was clarified by filtration. So, as a result of the Schiff base condensation we have obtained an erbium cryptate  $C_{39}H_{47}ErN_9O_6$  (MSB- $Er^{3+}$ ) complex.

The EPR spectra were recorded on a conventional X-band Bruker Elexsys E500 continuous-wave spectrometer operating at 9.5 GHz with 100 kHz magnetic field modulation. The investigated samples were in the form of fine powder. The first derivative of the power absorption spectra has been recorded as a function of the applied magnetic field. Temperature dependence of the EPR spectra in the 4–60 K temperature range was recorded using an Oxford Instruments ESP helium-flow cryostat. The EPR spectra were recorded at a microwave power of 0.63 mW. We have performed also observations on possible changes in the shape of the spectra with power increasing from 0.16 to 1.6 mW. The optimization of the spin Hamiltonian parameters and EPR data simulation were achieved with the SIMPOW software package [10].

## 3 Results and Discussion

In Fig. 1 a selection of registered EPR spectra taken at four different temperatures of 3.9, 6.1, 9.8 and 16.6 K is presented. Two main spectral components in a low magnetic field region ( $<200$  mT) are discernable. They are attributed to the  $Er^{3+}$  ions with an effective spin  $S = 1/2$ . The spectrum was observed only for temperatures lower than 60 K. The intensity of both spectral components decreases significantly with increasing temperature. There may appear a question



**Fig. 1.** Representative EPR spectra of the MSB-Er<sup>3+</sup> complex registered at different temperatures and comparison of the experimental (solid line) and calculated (dashed line) spectra at 3.9 K.

on the dispersion phenomenon which may be responsible for the shape of the EPR spectra. We measured the intensity of the EPR spectra as a function of microwave power and did not observe any changes with power. All registered EPR spectra were simulated by the SIMPOW computer program to extract important spectral parameters. The following effective spin Hamiltonian for an effective spin  $S = 1/2$  was used:  $\mathcal{H} = \beta B g S$ , where all symbols have their usual meaning. Calculated values of the three principal  $g_i$ -factors and the average  $g$ -factor (defined as  $g_{av} = (g_x + g_y + g_z)/3$ ) at the lowest registered temperature of 3.9 K and at the rather high temperature of 60 K are presented in Table 1. The  $g$ -values and anisotropic line widths are determined by solving the least-squares problem and comparison of the calculated spectra with a complete set of measured values in the SIMPOW program. Figure 2 presents the temperature dependence of the obtained anisotropic  $g_i$ -values (Fig. 2a) and anisotropic line widths (Fig. 2b).

The variety of magnetic behavior exhibited by the rare-earth ions may be considered by comparing their  $g$ -values. They reflect the nature of the ground state and how it is mixed with the low-lying excited states [11, 12]. In a cubic crystal field the 16-fold degenerated ground state of the Er<sup>3+</sup> ion splits into two doublets,  $\Gamma_7$  and  $\Gamma_6$ , with an effective spin  $S = 1/2$  and  $g$ -value of 6.8 and 6.0,

**Table 1.** Calculated values of principal  $g_i$ -factors and an average  $g_{av}$ -factor at several temperatures.

Temperature (K)	$g_x$	$g_y$	$g_z$	$g_{av}$
3.9	5.99	11.27	3.62	6.96
8.0	6.10	11.66	3.86	7.21
9.8	6.22	11.74	3.87	7.28
30	7.07	14.62	3.09	8.26
60	8.28	24.14	3.27	11.90

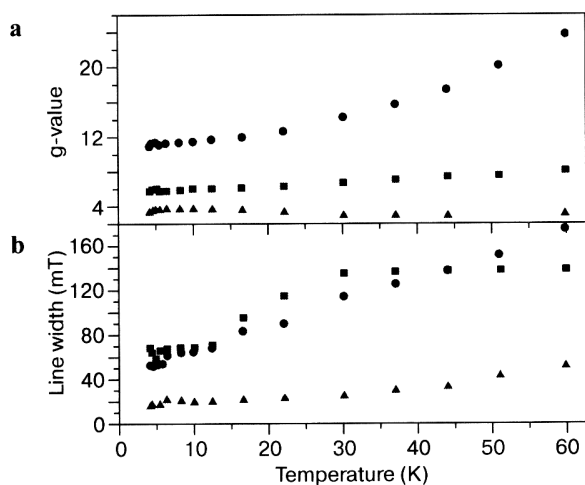


Fig. 2. Temperature dependence of the calculated anisotropic  $g_i$ -factors (a) and anisotropic line widths  $\Delta B_i$  (b) ( $i = x$  [■],  $y$  [●],  $z$  [▲]).

respectively, and into three  $\Gamma_8$  quartets, each with an effective spin  $S = 3/2$ , generating an anisotropic Zeeman interaction [13]. In a sufficiently strong low-symmetry crystal field the quartets split into doublets. It has often been found that when the symmetry of the crystal field becomes noncubic the average  $g$ -value remains close to that of the parent state  $\Gamma_6$  or  $\Gamma_7$  [14, 15]. The principal and average  $g_{av}$ -values for the MSB-Er<sup>3+</sup> complex at several temperatures are given in Table 1. At the lowest investigated temperature,  $g_{av}$  is closer to that for  $\Gamma_7$  than that for  $\Gamma_6$ , but the difference from the theoretical value is significant and increases at higher temperatures. This may indicate a large admixture of the MSB complex wavefunction to the Er<sup>3+</sup> ground state. As it is shown further this fact would have a pronounced effect on the temperature dependence of the spin system susceptibility. Lack of visible hyperfine structure associated with the 23% abundant <sup>167</sup>Er isotope with  $I = 7/2$  should be attributed to a weak signal-to-noise ratio.

The temperature dependence of the spin Hamiltonian parameters has revealed the presence of three temperature regions with different behavior. At 5 K the anisotropic  $g$ -factors reach local maximum values and the line widths reach local minimum values. In the 5–13 K temperature range the line width and  $g$ -factor remain constant, and above 13 K a strong increase of  $g_y$ -factor and  $\Delta B_y$  line width is observed. The most important point here is to note that the values of  $g$ -factors in the whole temperature range are above 2.0. It could be explained by assuming that the EPR signal arises from monomeric erbium ions. The temperature dependence of  $g$ -factor evidences an increasing magnetic anisotropy of the complex with increasing temperature.

A very important spectroscopic parameter that can be calculated from the EPR spectrum is the integrated intensity  $I$  (Fig. 3a), defined as the area under the absorption resonance line and proportional to the magnetic susceptibility of the

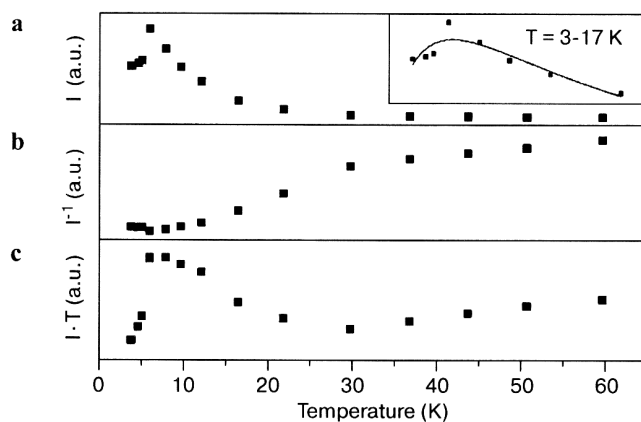


Fig. 3. Temperature dependence of the integrated intensity  $I$  (a), reciprocal integrated intensity  $I^{-1}$  (b), and the product  $I \cdot T$  (c). The inset in a shows the best fit to Eq. (1) in the low-temperature range.

investigated spin system. The study of the temperature dependence of  $I$  could yield information on magnetic interactions between the spin species. Inspection of Fig. 3 shows a maximum of the integrated intensity at 6 K, while above and below this temperature the EPR signal significantly decreases. These changes do not agree with a Curie–Weiss relation. As the product  $T \cdot I$  is proportional to the square of an effective magnetic moment, Fig. 3c indicates that on sample cooling from 60 to 30 K the magnetic moment slightly decreases. In the second temperature range between 30 and 5 K the effective magnetic moment appreciably increases. Thus the dominating interaction between the complexes above 30 K is of the antiferromagnetic type, while below 30 K it is of the ferromagnetic type. At the temperature  $T = 30$  K the crossover of the magnetic interactions takes place.

In the inset of Fig. 3a the temperature dependence of the integrated intensity near its maximum is also presented. This dependence suggests that the EPR spectrum arises from the excited states. It could be analyzed in terms of the following equation

$$I(T) = \alpha \exp(-T_0/T)/T, \quad (1)$$

where  $T_0$  is the difference of energy (expressed in kelvins) between the ground (nonmagnetic) and the excited states. The analysis shows that the ground state is about 6.3 K below the excited state that produces the EPR signal [16]. In a recently published paper on magnetic studies of the Gd(III) tripodal Schiff base complex [8] the existence of clusters with nonmagnetic  $S = 0$  ground state and magnetic excited states has been deduced from a steep rise of the magnetic moment with the increasing temperature. As a single  $\text{Er}^{3+}$  ion could not produce a nonmagnetic ground state, another explanation of the observed temperature dependence of the integrated intensity (magnetic susceptibility of the investigated spin system) has to be found. We propose to include the ions in the coordination sphere of the  $\text{Er}^{3+}$

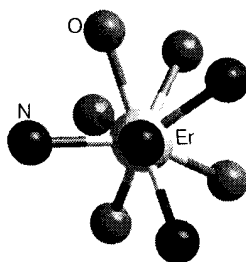


Fig. 4. Coordination sphere of the  $\text{Er}^{3+}$  cation deduced from the infrared spectrum and molecular mechanics simulation [17].

ion (Fig. 4) into consideration of a complex magnetic system that produces the observed EPR signal. The admixture of wavefunctions of the surrounding ions (especially large at high temperatures) into the wavefunction of the  $\text{Er}^{3+}$  ion may produce a nonmagnetic ground state of the whole complex.

In one of our previous reports [17] using the Fourier transform infrared and thermogravimetric and differential thermal analyzer techniques we confirmed the complexation of the MSB ligand with erbium, its monomeric [1:1] nature, and the presence of  $\text{NO}_3$  and one water molecule in an inner sphere of the complex. The coordination sphere of the  $\text{Er}^{3+}$  cation contains nine ions (Fig. 4). There are three O and four N atoms from the MSB ligand molecule and two oxygen atoms of the nitrate group. The other part of the MSB ligand interacts with one water molecule. Due to the  $\text{Er}^{3+}$  coordination number nine, the cation achieves an almost symmetrical coordination sphere of three-capped trigonal prism geometry [3].

The presence of a nitrate group and a water molecule in the vicinity of the  $\text{Er}^{3+}$  ion should be reflected in the temperature dependence of magnetic properties of the MSB- $\text{Er}^{3+}$  complex. As the dynamics of these molecular units changes with temperature due to freezing of their specific modes of motion, appropriate changes are expected in EPR line widths and  $g$ -factors. Thus, the temperatures of 13 and 30 K at which the changes in magnetic interactions were observed could be correlated with subsequent changes in the motion of the nitrate and water molecules.

The identification of the ground and the excited states, as well as the explanation of the temperature dependence of the  $g$ -factor, are impossible at this stage of investigation since the structure of the complex is very complicated. A deeper insight into the energy structure of the complex would require growing of a single crystal and its subsequent investigation by EPR technique to determine the detailed magnetic anisotropy.

#### 4 Conclusions

Variable-temperature EPR study of the MSB- $\text{Er}^{3+}$  complex revealed a low-symmetry site of the  $\text{Er}^{3+}$  cation and a complicated pattern of magnetic interactions in this system. Computer analysis of the registered EPR spectra allowed calcula-

tion of the thermal behavior of important spectral parameters and correlation of the observed changes with the dynamics of molecular entities in the nearest vicinity of the paramagnetic center. The low-temperature drop of the integrated intensity (below 6 K) is the result of the existence of a nonmagnetic ground state lying 6.3 K below the excited states that produces the observed EPR signal.

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