Magnetic and spectroscopic properties of gadolinium tripodal Schiff base complex

G. Leniec [a,*], S.M. Kaczmarek [a], J. Typek [a], B. Kołodziej [b], E. Grech [b], W. Schilf [c]

[a] *Institute of Physics, Szczecin University of Technology, Al. Piastów 17, 70-310 Szczecin, Poland*
[b] *Department of Inorganic and Analytical Chemistry, Szczecin University of Technology, Al. Piastów 42, 70-310 Szczecin, Poland*
[c] *Institute of Organic Chemistry PAS, Kasprzaka 44/52, 01-224 Warsaw, Poland*

Abstract

Gadolinium(III) tripodal Schiff base (tris(((5-chlorosalicylidene)amino)ethyl)amine) complex has been obtained and investigated by infrared spectroscopy (IR), magnetic susceptibility, and electron paramagnetic resonance (EPR) methods. Comparison of IR bands in ligand and gadolinium complex confirmed the formation of the gadolinium complex and allowed to propose its structure. Both electron ionization and electron spray molecular spectroscopy spectra confirmed the [1:1] proportion of a ligand to metal in gadolinium tripodal Schiff base complex sample. IR spectroscopy and TG—DTA excluded the presence of water molecule in the metal coordination sphere. X-ray powder analysis applying Fullprof computer program has shown that the investigated sample was monophase with the monoclinic symmetry of the unit cell having the lattice constants: $a = 10.028(4)$ Å, $b = 13.282(5)$ Å, $c = 21.20(1)$ Å and $\beta = 101.58(4)°$. Space group $P21/c$, $Z = 4$. EPR spectra of the complex have been registered in the 4—300 K temperature range. Each spectrum has been fitted using EPR—NMR computer program and the values of the spin-Hamiltonian parameters at each temperature have been calculated. Temperature dependence of the integrated intensity of the EPR spectrum allowed revealing the magnetic interactions in the spin system of this compound. Comparison of the temperature dependence of dc magnetic susceptibility (χ) and EPR susceptibility (χ_{EPR}) showed significant differences between these quantities due to the presence of short-lived clusters with a non-magnetic ground state.
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1. Introduction

The coordination chemistry of lanthanide(III) ions has been extensively studied in the recent years because the resulting complexes can be conveniently employed as useful devices or probes in a variety of fields, ranging from solid state to analytical chemistry, hydrometallurgy, biology, medicine, etc. [1–3]. The great interest in synthetic macrocycles and macroacycles and their corresponding metal complexes is related to the fact that they can mimic naturally occurring macromolecules in their structural features. The formation of tripodal complexes depends significantly on the dimension of the internal cavity, on the rigidity of the ligand, on the nature of its donor atoms and on the complexing properties of the counterion. For tripodal compounds, like podands, higher flexibility of arms and complexation ability grows with the ionic radius of rare-earth ions. These compounds have been designed to form [1:1], [1:2] and more metal ions complexes [4–6].

The tripodal Schiff base ligands have gained favor due to both their relatively straightforward synthesis and their multidentate nature which results in very high binding constants for many d- and f-metals [7–9]. Schematic structure of the ligand used in our investigations, designated as 33T, is presented in Fig. 1.

Over the last decade, the sustained research activity devoted to the lanthanide ions and their complexes has stemmed

* Corresponding author.
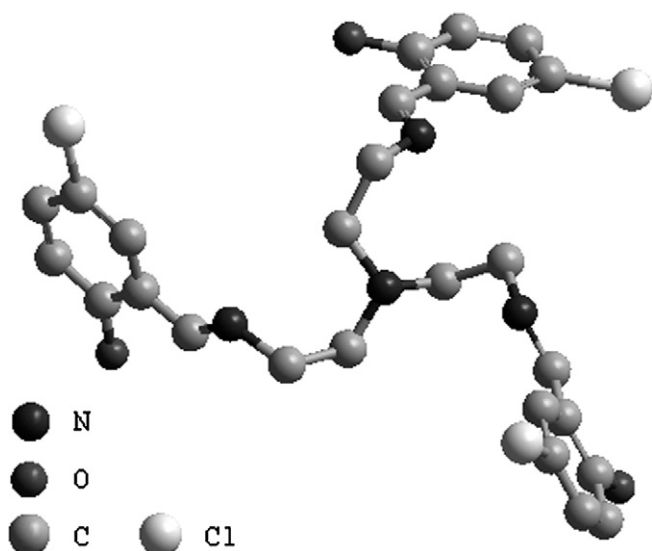 *E-mail address:* taran@ps.pl (G. Leniec).

Fig 1. Schematic representation of the structure of 33T ligand (without hydrogen atoms).

in part from the successful applications of these compounds in medicine and in biology. Because of its high magnetic moment and its long relaxation times, gadolinium is used to improve the contrast of magnetic resonance images [10,11]. Moreover, the long lifetimes of excited states of some lanthanides allow time-gated measurements of the luminescence of ions without interferences from biological molecules. Finally, lanthanide ions are effective catalysts for the hydrolytic cleavage of RNA [12]. All these applications require that the lanthanide ions are used as stable chelates and the ligands featuring anchor groups are preferred to ensure that the metal ions always remain tethered to a biologically active macromolecule. In most cases, tripodal ligands and their metal complexes are very stable and kinetically very inert [13].

In this paper, we report synthesis of the gadolinium tripodal Schiff base complex (designated as 33TGd) and study its spectroscopic properties using infrared spectroscopy (IR), mass spectroscopy (MS), electron paramagnetic resonance (EPR), and dc magnetic susceptibility methods. Analysis of the obtained EPR spectra in a wide temperature range would allow us to draw conclusions on the structure and magnetic properties of the investigated complex.

2. Experimental

Tris(((5-chlorosalicylidene)amino)ethyl)amine ligand was obtained based on method presented in Refs. [7,8]. Tris(((5-chlorosalicylidene)amino)ethyl)amine gadolinium complex (33TGd) was obtained according to a known method [6]. Tris-(2-aminoethyl)amine (tren) was added to a solution of $Gd(CF_3SO_3)_3$ in hot methanol (70 cm^3) and refluxed for 10 min. Then 5-chlorosalicylaldehyde in methanol (30 cm^3) was added to this solution and refluxed for 2 min. The molar ratio of tren, $Gd(CF_3SO_3)_3$, 5-chlorosalicylaldehyde was 2:1:3. A yellow solid was precipitated upon cooling for 6 h. The obtained crystalline powder was separated by filtration. Yield: 76%. Anal. Calcd for $C_{27}H_{24}N_4O_3Cl_3$ (716.13): C, 45.29; H, 3.38; N, 7.82. Found: C, 44.37; H, 3.34; N, 7.46 and C, 44.21; H, 3.39; N, 7.64.

The IR spectra of a solid compound were recorded on a Brüker FT-IR IFS 113v spectrophotometer in the region of 3500–400 cm^{-1} applying 33T complex powder mixed with KBr and pressed into pellets and complex powder immersed in poly(chlorotrifluoroethylene) emulsion placed between CaF$_2$ plates. The spectra of the Schiff base ligand and gadolinium complex were recorded at room temperature (RT) with the resolution of 2 cm^{-1}.

Static magnetic susceptibility measurements were performed on a Quantum Design MPMS SQUID magnetometer
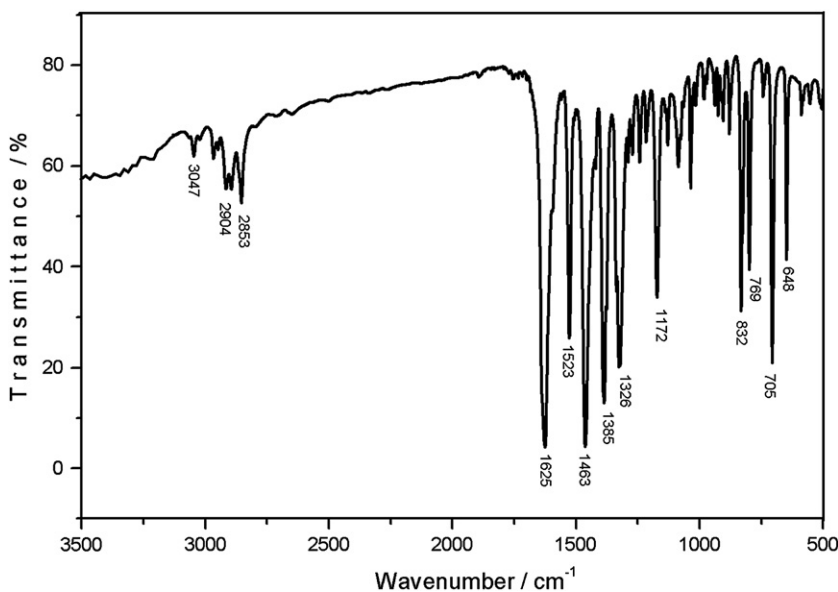

Fig 2. RT IR spectra of 33TGd complex immersed in poly(chlorotrifluoroethylene) emulsion placed between CaF$_2$ plates.

in the temperature range of 2−300 K and magnetic fields up to 50 kOe in zero-field-cooled (ZFC) mode. The diamagnetic contribution of the compound was estimated using Pascal's co-efficients, while the contribution of the support cell was inde-pendently measured and subtracted.

MS analysis was performed using the following devices: the electron ionization (EI) mass spectrum of 33TGd sample has been registered using AMD 604 system (EI 70 eV, $T = 346$ K); for electron spray (ES) mass spectrum the Mariner of PE Biosys-tems spectrometer, operating with TOF detection system has been used (MeOH solution, positive ions, NP = 400).

The DTA measurements were conducted by using the F. Paulik−L. Paulik−L. Erdey derivatograph (MOM, Budapest, Hungary). TG−DTA was performed in N_2 atmosphere with a heating rate of 10°/min in the range of 20−500 °C. The mass of the investigated powder form sample was 21 mg.

The XRD examination was performed by using the DRON-3 diffractometer (Bourevestnik, Sankt Petersburg, Russia) ap-plying $CoK\alpha$/Fe radiation. The identification of individual phases was carried out on the ground of the consistence of the obtained diffraction patterns with the data supplied by JC PDF files [6]. Exact positions of diffraction lines were de-termined by the internal standard method. The crystallo-graphic parameters were determined by using the FullProf computer program (pattern matching).

The EPR spectra were recorded using Brüker E 500 spec-trometer operating at X-band microwave frequency equipped with TE_{102} cavity and 100 kHz field modulation. The investi-gated sample in the form of loose powder was used and during the measurements it was placed in quartz tube 4 mm in diam-eter. As usual, the first derivative of powder absorption has been determined as a function of applied magnetic field. Tem-perature dependence of the EPR spectrum was registered using an Oxford Instruments ESP helium-flow cryostat working in the 3−300 K temperature range. Determination and optimiza-tion of the spin-Hamiltonian parameters and EPR data simula-tion have been done using the software package EPR−NMR [14].

3. Results and discussion

In Fig. 2 IR absorption spectrum of the gadolinium Schiff base complex (33TGd) is presented. The most characteristic vibrational wave numbers of gadolinium podante mixed with KBr had been compared with those of a free ligand mixed with KBr and are listed in Table 1.

The $\nu(C=N)$ stretching bond in the ligand was observed at 1635 cm^{-1}. In the Gd(III) complex, this bond was shifted to-wards lower energy region and observed at 1625 cm^{-1}. This indicates that the nitrogen of the azomethine group is coordi-nated to the rare earth ion. The phenolic $\nu(OH)$ stretching bond in the ligand was observed at 3436 cm^{-1}. The $\nu(OH)$ stretch-ing bond in Gd(III) complex was observed at 3431 cm^{-1} in case of KBr pellets, whereas using CaF_2 plates this bond was not observed (see Fig. 2, bottom panel). This indicates that oxygen of the phenolic OH group is coordinated to the rare earth ion. Consequently, the connection between metal

and ligand takes place between nitrogen of the azomethine group and oxygen of the phenolic group. The coordination number of the gadolinium is seven, it means that the gadoli-nium ion is involved in coordination with three oxygen atoms as donor atoms and four nitrogen atoms. Moreover, this con-firms the formation of a complex.

TG−DTA has revealed that up to 699 K there is not a signif-icant loss of a mass of the sample. Thus the TG−DTA profile confirms no water coordination of the metal ion in the inves-tigated complex.

In the EI spectrum of 33TGd complex the molecular peak of $m/e = 717$ was observed that corresponds to a compound in which three protons have been replaced by one gadolinium atom. The isotope pattern of molecular peak is typical for the compound with one gadolinium atom. In the electron spray spectrum the main peak, with the isotope pattern similar to the above mentioned molecular peak, was observed at $m/e = 718$ and assigned to the single-protonated species contain-ing one gadolinium atom. Both MS spectra confirm the [1:1] proportion of ligand to metal in the 33TGd sample.

X-ray powder diffraction measurements have shown that the investigated 33TGd sample has a monoclinic symmetry with the lattice parameters: $a = 10.028(4)$ Å, $b = 13.282(5)$ Å, $c = 21.20(1)$ Å and $\beta = 101.58(4)°$ and cell volume $V = 2751.9(2)$ Å^3, space group $P21/c$, $Z = 4$. The diffraction pattern of this sample revealed the absence of any additional diffraction lines from other phases.

Results of the dc magnetic susceptibility measurements are presented in Fig. 3. For the whole investigated temperature range the experimental data could be fitted very well to the Curie−Weiss law, $\chi = C/(T - \theta)$, with the Curie−Weiss tem-perature $\theta = -0.191(1)$ K. The solid line in Fig. 3 represents the best fit to the experimental data according to that law. The magnetic data were also plotted as $1/\chi$ versus T, yielding linear behaviour. A small negative value of the paramagnetic

Table 1
Characteristic absorption bands observed in both Schiff base ligand and gado-linium podand mixed with KBr

Assignment	Schiff base ligand (cm^{-1})	Gadolinium podand (cm^{-1})
δ_{ring}		648
		705
		797
$\gamma(C-H)_{aromatic}$		832
	815	
$\nu(C-C)$	1089	
	1034	
		1172
$\nu(C-O)_{phenolic}$	1200	
	1270	
		1326
$\delta_s(CH_2)$	1367	
$\nu(C-N)_{aliphatic}$	1474	1463
$\nu(C=C)_{aromatic}$		1523
	1608	Superposition
$\nu(C=N)$	1635	1625
$\nu(CH_2)$	2950−2816	2967−2853

ν, Stretching; δ, in-plane bending; γ, out of plane bending; subscript s, scissoring.
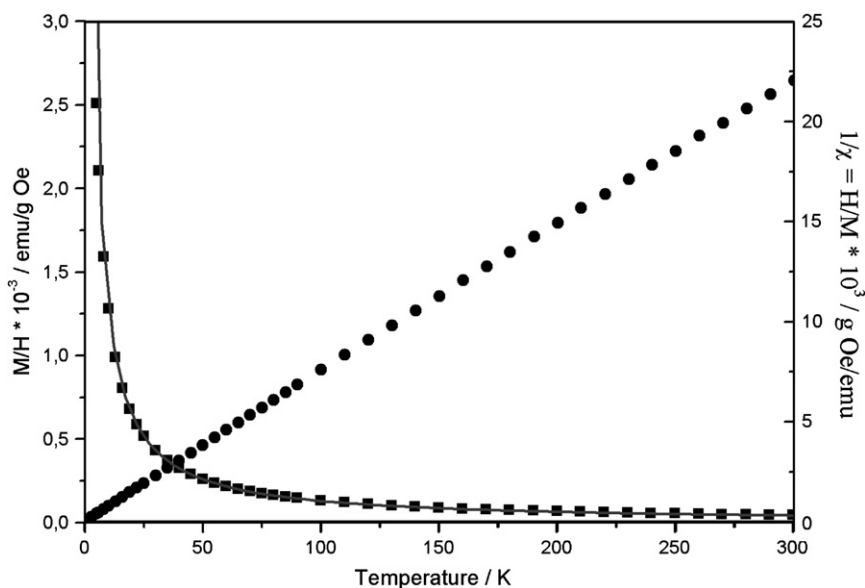
Fig. 3. Temperature dependence of magnetic susceptibility (for $H = 0.1$ kOe).

Curie–Weiss temperature indicates only a very weak antiferromagnetic interaction between the Gd^{3+} ions. Such behaviour could be also explained by the presence of a small amount of magnetically ordered (antiferromagnetic) clusters. From the Curie constant C the effective magnetic moment per gadolinium ion $\mu_{eff}^2 = 3Ck/\mu_B^2 N$, where k is the Boltzmann constant, μ_B the Bohr magneton and N is the Avogadro's number, could be calculated. The effective magnetic moment equals $8.628(1)\mu_B$, which is higher than the spin only value expected for the free Gd^{3+} ion ($\mu_{eff} = g[S(S+1)]^{1/2} = 7.94\mu_B$). This discrepancy could indicate on the existence of a strong spin–orbit coupling. There is no evidence on the presence of an antiferromagnetic phase in this compound down to 2 K.

Fig. 4 shows magnetization variations of the sample in an external magnetic field for three different temperatures. The solid line is the Brillouin function for $J = 7/2$. The effective magnetic moment calculated from the saturation magnetization is $\mu_{eff} = 8.434(6)\mu_B$ and is lower than the value obtained from susceptibility measurements. This discrepancy could be explained by postulating the existence, besides the majority of isolated Gd^{3+} complexes, of relatively small number of gadolinium clusters [15].

Fig. 5a and b presents the powder EPR spectra of the 33TGd complex for a few selected temperatures in the 3–300 K range. The EPR signal consists of a main, intense, asymmetric, and broad line with unresolved structure, centered at $g \sim 2$, and many additional weaker lines at lower ($g \sim 6$) and higher ($g \sim 1.5$) magnetic fields. The intensity of the spectrum varies significantly with temperature. The amplitude of the main peak centered at $g \sim 2$ decreases with temperature decrease from RT down to 3 K.

Using computer simulation of the experimental EPR spectra it is possible to extract the values of the spin-Hamiltonian parameters required for the determination of structural information of the complex. For Gd(III) ions having half-filled f

shell with seven electrons and the ground state $^8S_{7/2}$, the spin Hamiltonian should contain spin terms of the type BS (matrix g), S^2 (matrix D) as well as parameters associated with the high-spin terms of the type S^4 and S^6. The following spin Hamiltonian was used to generate the powder EPR spectra:

$$H_s = \mu_B SgB + SDS + \sum_{m=-l}^{l} B_l^m O_l^m(S), \qquad (1)$$

where the first term is the electronic Zeeman term, the second one is the fine structure electronic quadrupole term and the third one contains terms of S^4 and S^6 in Stevens notation. In Eq. (1) B is the magnitude of the applied magnetic field, $O_l^m(S)$ are Stevens operators of m degree, and B_l^m are Stevens
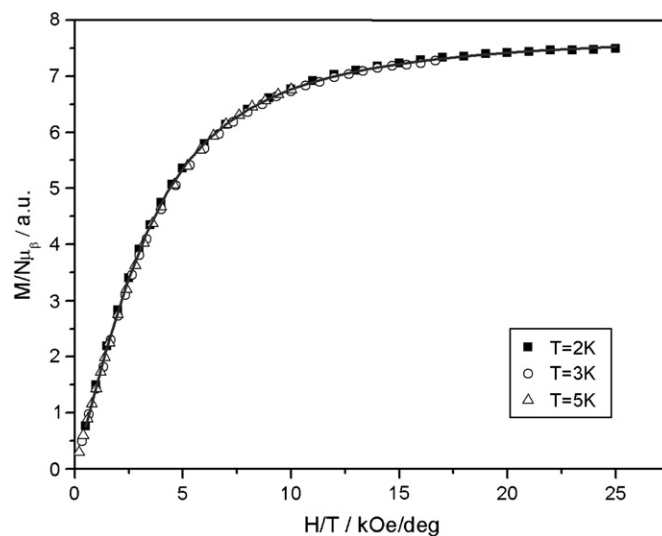

Fig. 4. Magnetization of the investigated sample in an external magnetic field for three temperatures. The solid line is the Brillouin function for $J = 7/2$.
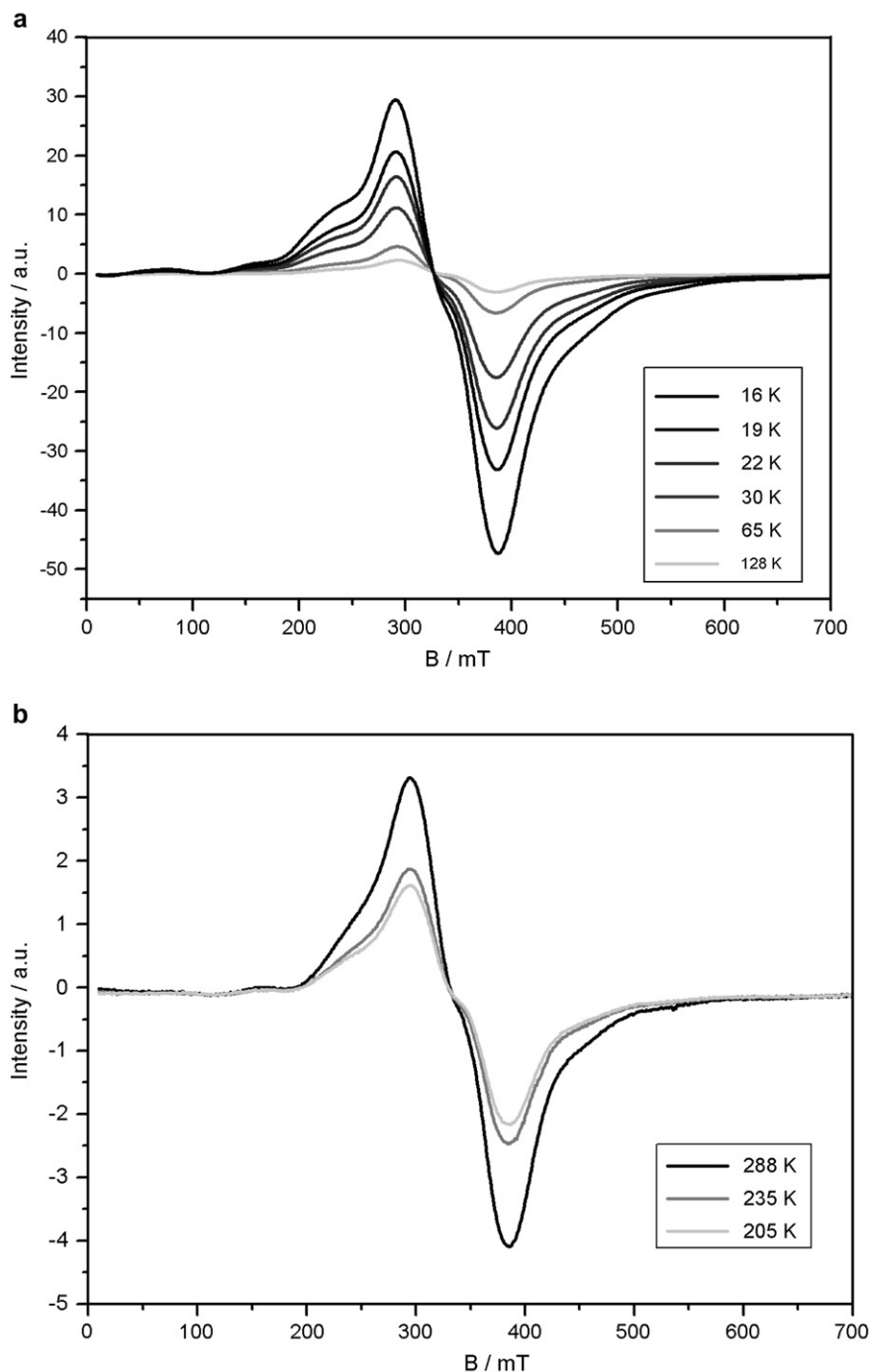
Fig. 5. EPR spectra of 33TGd complex at selected temperatures: (a) high-temperature range ($T > 100$ K); (b) low-temperature range ($T < 100$ K).

parameters [16]. The number of non-zero B_l^m parameters depends on the site symmetry of paramagnetic centre [17].

All registered EPR spectra of the investigated complex at different temperatures have been simulated using EPR–NMR computer program in order to study thermal changes of the spin-Hamiltonian parameters. As an example, Fig. 6 presents simulated (upper panel) and experimental (middle panel) spectra of the 33TGd complex at 288 K. The accordance between these two spectra is satisfactory, what can be evidenced by the lowest panel in Fig. 6, which shows their difference, with

no apparent structure discernable. In Table 2 the calculated spin-Hamiltonian parameters for $T = 3$ K and at RT, are given. The presence of three different g_i and non-zero values of B_2^0, B_2^2, B_4^0, B_4^2, B_4^{-2}, B_4^4, B_4^{-4} and B_6^0 indicates monoclinic symmetry of the crystal field at the Gd(III) site. The accuracy of the calculated parameters has been estimated by varying the values of parameters and observing changes in the simulated spectrum. If the difference between the simulated and experimental spectrum revealed a significant spectral feature then that set of parameters was judged as not appropriate. This method is not
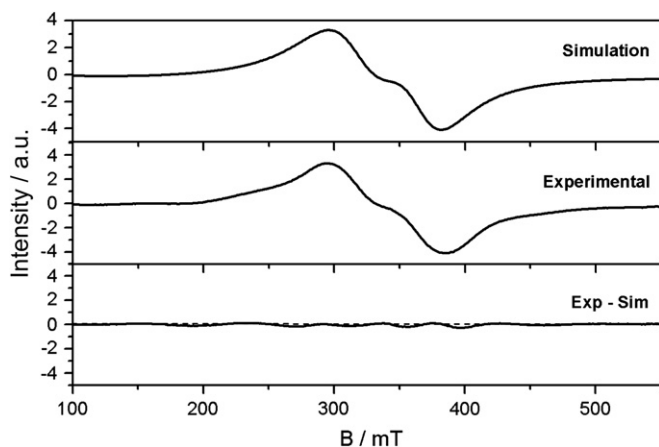
Fig. 6. Simulated (top panel), experimental (middle panel) and the difference (lower panel) of the EPR spectra of 33TGd complex at $T = 288$ K.

dependence of χ_{EPR} could yield information on magnetic interactions between the spin species. Fig. 7 displays the results of the temperature studies of χ_{EPR} for the 33TGd complex. The upper panel in Fig. 7 shows the temperature dependence of χ_{EPR}, the middle panel reveals the reciprocal integrated intensity χ_{EPR}^{-1}, and the lower one presents the product $T\chi_{EPR}$ that is proportional to the square root of the effective magnetic moment. Inspection of Fig. 7 indicates that there is no magnetically ordered state in the 33TGd complex in this temperature range. As temperature is decreased from RT, I_{int} decreases slightly down to ~ 190 K, and on further cooling starts to increase at accelerated rate. It is clear that the thermal changes of I_{int} could not be described by a simple Curie–Weiss relation, in the whole investigated temperature range. Below 130 K there is a linear dependence of I_{int}^{-1} (Fig. 7, middle panel), and in that range the Curie–Weiss relation holds with the Curie–Weiss temperature $\theta_{EPR} = 10$ K. It suggests there is a ferromagnetic interaction between 33TGd complexes below 130 K. On the other hand, in the high-temperature range, $T > 190$ K, the situation is quite different. The lower panel in Fig. 7 indicates that the magnetic moment decreases significantly as the temperature is lowered from RT. Thus, at high temperatures, there is a strong antiferromagnetic interaction between at least part of the Gd(III) complexes. EPR measurements confirm that there is no long-range magnetic order in the investigated compound, but only magnetic interactions between the paramagnetic centers. To explain the observed behaviour of the temperature EPR spectra at least two options have to be considered. The first one is the existence of the high-spin low-spin transition and the occurrence of the excited low-spin form at room temperature. Such a transition would require a very strong change of the crystal field acting on the paramagnetic complex. This has not been observed in the thermal dependence of crystal field parameters. Besides, the observed thermal changes of the B_l^m parameters do not correlate with the changes of the effective magnetic moment. Another possibility that should be considered is the existence of the short-lived clusters. The antiferromagnetic interaction between neighboring complexes might favor formation of a certain number of short-lived (on the time scale of the EPR

entirely reliable (as in case of other methods used for powder analysis), but the relative error of the estimated non-zero spin-Hamiltonian parameters should not exceed 20%. For these parameters, which were calculated to have zero value, the error is lower than 1 Gs for the B_2 parameters, 0.5 Gs for the B_4 parameters and 0.03 Gs for the B_6 parameters.

Thermal dependence study of the spin-Hamiltonian parameters showed that g_i-factors do not change with temperature, while many B_l^m ($l = 2, 4, 6$) parameters displayed rather significant temperature dependence. The calculated spin-Hamiltonian parameters B_l^m ($l = 2, 4, 6$) showed significant changes with temperature decrease from RT. For low and high temperatures the values of these parameters are listed in Table 2. All the other B_l^m parameters have zero value and didn't change with temperature.

A very important spectroscopic parameter that can be calculated from the EPR spectrum is the integrated intensity. It is defined as the area under the absorption resonance line (not the first derivative of absorption line usually registered) and is proportional to the magnetic susceptibility of the investigated spin system. The integrated intensity of the EPR spectrum will be designated as χ_{EPR}. The study of the temperature

Table 2

Values of the spin-Hamiltonian parameters for the 33TGd complex at 3 and 288 K

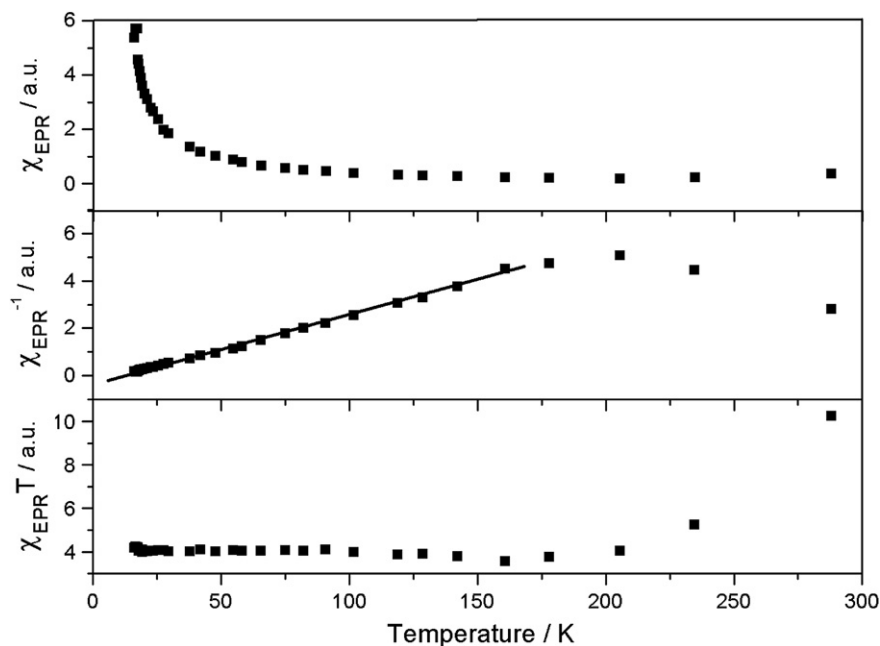| g Tensor	Stevens parameters (Gs)								
	m	B_2^m		m	B_4^m		m	B_6^m	
		$T = 3$ K	$T = 288$ K		$T = 3$ K	$T = 288$ K		$T = 3$ K	$T = 288$ K
$g_{xx} = 1.989$		-86	-86.5	0	0.2	-0.12	0	0.07	0.06
$g_{yy} = 1.999$	0	-86	-86.5						
$g_{zz} = 2.000$	1	0.0	0.0	1	0.0	0.00	1	0.00	0.00
	2	6.5	26.5	2	3.0	1.00	2	0.00	0.00
	-2	0.0	0.0	3	0.0	0.00	3	0.00	0.00
	-1	0.0	0.0	4	1.5	3.00	4	0.00	0.00
				-4	2.0	2.00	5	0.00	0.00
				-3	0.0	0.00	6	0.00	0.00
				-2	3.5	3.00	-6	0.00	0.00
				-1	0.0	0.00	-5	0.00	0.00
							-4	0.00	0.00
							-3	0.00	0.00
							-2	0.00	0.00
							-1	0.00	0.00

Fig. 7. Temperature dependence of the EPR integrated intensity for the 33TGd complex (upper panel), of the reciprocal integrated intensity (middle panel) and the product TI_{int} (lower panel).

spectroscopy, $\tau \sim 10^{-10}$ s) clusters with non-magnetic $S = 0$ ground state and magnetic excited states. As the temperature decreases from RT, the population of the excited states decreases and the population of the non-magnetic state increases, decreasing in consequence the total magnetic moment of the system. Static magnetic susceptibility measurements in that temperature range didn't reveal any contribution from these short-lived clusters what is understandable as that method registers only static magnetic entities.

4. Conclusions

IR measurements have evidenced the formation of the 33TGd complex, in which the nearest neighborhood of Gd(III) consists of seven atoms: three oxygen and four nitrogen. The local symmetry at the Gd(III) site is rather low (C_1) as proved by the presence of many non-zero parameters in the spin Hamiltonian. Temperature dependence of the EPR integrated intensity indicates that there is no magnetically ordered state in this compound down to temperature of 3 K. In the high-temperature range, $T > 190$ K, a strong antiferromagnetic interactions between Gd(III) complexes are evidenced by decreasing magnetic moment with the temperature decrease. This interaction might favor formation of short-lived clusters with a non-magnetic ground state.

Acknowledgements

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