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Spectroscopic and magnetic properties of a gadolinium macrobicyclic complex

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Abstract
As a result of Schiff base condensation, gadolinium cryptate has been synthesized and investigated by infrared (IR) spectroscopy and electron paramagnetic resonance (EPR) technique. Comparison of IR bands in a ligand and the gadolinium complex confirmed the formation of the gadolinium cryptate complex. IR and thermogravimetry-differential thermal analysis (TG-DTA) analyses indicate the presence of two water molecules in the inner sphere of the complex. Mass spectroscopy investigations confirmed a monometallic substitution of the Gd^{3+} ion into the macrobicycle ligand. EPR spectra of the complex have been registered in the 3–300 K temperature range. Each spectrum has been simulated using the EPR–NMR computer program and the values of the spin Hamiltonian parameters at each temperature have been calculated. The thermal dependence of the spin Hamiltonian parameters has been investigated. The temperature dependence of the integrated intensity of the EPR spectrum revealed the magnetic interactions in the spin system of this compound. No long-range magnetic order has been detected in the 3–300 K range, but a strong antiferromagnetic interaction in the high-temperature range, above 160 K, has been observed.

1. Introduction

The macrobicyclic compounds are interesting because of their ability to form complexes with transition metal ions and rare earths. The design and synthesis of macrobicyclic ligands and their lanthanide complexes are important in applied chemistry, biochemistry and technology.

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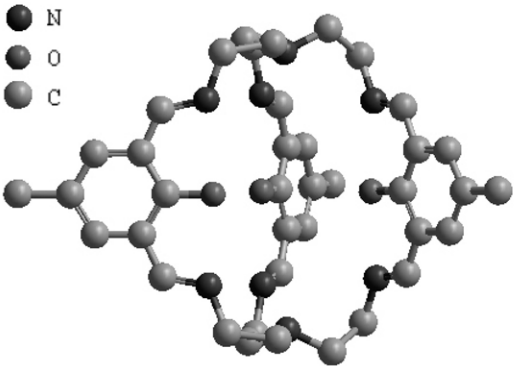

Figure 1. Schematic diagram of the 1T ligand structure (without hydrogen atoms).

These complexes are often applied for the separation of selected metals, as catalysts and supramolecular devices. Moreover, the related d- and especially 4f-metal ion complexes are used as fluorescent probes in biological systems, as the contrast media in medical diagnostics, and as synthetic enzymes to split the chain of nucleic acid. They are often applied in such medical treatments as arteriosclerosis and radioimmunology [1–6].

The formation of macrobicyclic complexes to act as suitable chelating agents for rare-earth ions depends significantly on (a) the dimension of the internal cavity and the goodness of fit of the cation in the ligand cavity (rigidity of macrobicycle), (b) the complexing properties of the counterion, (c) the nature of the donor atoms [7, 8]. These macrobicyclic compounds allow the formation of both monometallic (1:1) and bimetallic (1:2) lanthanide cryptates and the encapsulation of the lanthanide ion into the cavity [4]. These lanthanide cryptates are attractive due to their ability to bind two or more metal ions in close proximity [5]. Avecilla *et al* demonstrated previously the ability of trivalent lanthanide ions to promote the formation of Schiff base axial macrobicyclic ligands [9–11].

There are only a few successful methods of preparation of macrobicycle complexes. One of them involves the formation of macrobicycle Schiff base complexes, owing to their relative uncomplicated preparation through the condensation reaction of 2-hydroxy-5-methylisophtalaldehyde and lanthanide (III) trifluoromethanesulfonate with tris(2-aminoethyl)amine. This method was used to synthesize the complex studied in this paper. Figure 1 presents a schematic diagram of the ligand used.

It should be mentioned that monometallic cryptates with an axial cryptand L, $N[(CH_2)_2N{=}CH{-}R{-}CH{=}N(CH_2)_2]_3N$ also designated as $R{=}m\text{-}C_6H_2OH\text{-}2\text{-}Me\text{-}5$, and with its tert-butylated analogue have been previously obtained for LN = Sc, Y, Gd, Eu, Tb and Dy by transmetallization of the sodium derivatives [6].

There are many papers reporting on the three-dimensional lanthanide complexes (see e.g. [2]). But, so far, there are only a few reports on the electron paramagnetic resonance (EPR) spectra and the spin Hamiltonian parameters of these complexes [12]. The high sensitivity of EPR spectroscopy makes this method an effective tool for the study of the magnetic properties of gadolinium complexes. Besides EPR measurements, IR spectra analysis also seems to be an indispensable tool for structure (bonds) description. The assignment of the most important vibrational modes helps in confirmation of the complexation of the Schiff base ligand with a gadolinium ion. Mass spectroscopy could give evidence on the type of form of the macrobicycle complex, while thermogravimetric analysis could indicate whether the cryptate has a water molecule in the inner coordination sphere.

In this paper we report the synthesis of gadolinium cryptate as a result of Schiff base condensation and study its spectroscopic properties using EPR, IR, TG-DTA and mass spectroscopy. Analysis of the obtained EPR spectra in a wide temperature range allowed drawing conclusions on the structure and magnetic properties of the investigated complex.

2. Experimental details

The synthesis of the gadolinium complex (designated as 1TGd) was performed as follows. Tris-(2-aminoethyl)amine (tren) (8 mmol) was added to a solution of $Gd(CF_3SO_3)_3$ (4 mmol) in hot methanol (70 cm^3) and refluxed for 10 min. Then 2-hydroxy-5-methylisophtalaldehyde (12 mmol) in methanol (30 cm^3) was added to this solution and refluxed for 2 min. A yellow solid had precipitated upon cooling for 6 h. The crystalline powder was clarified by filtration. Yield: 88%.

The IR spectra of a solid compound were recorded on a Bruker FT-IR IFS 113v spectrophotometer in KBr pellets. The spectra of the Schiff base ligand and gadolinium complex were recorded at room temperature (RT) with a resolution of 2 cm^{-1}.

The DTA measurements were conducted by using a Mettler, Star^e SW 8.10 derivatograph. TG-DTA analysis was performed in a N_2 atmosphere with a heating rate of 10 K min^{-1} in the range 300–600 K. The mass of the investigated powder form sample was 390 000 mg.

To tests on the monometallic or bimetallic substitution of the Gd^{3+} ion into the macrobicyclic ligand the mass spectrometry investigations were performed using an AMD 604 mass spectrometer for electron ionization (EI) experiments. Since no molecular peak was observed in the EI spectrum the additional electron spray spectrum was recorded using an API 365 PE Sciex mass spectrometer equipped with a double quadruple detection system.

The EPR measurements were performed with a conventional X-band Bruker ELEXSYS E 500 CW-spectrometer operating at 9.5 GHz with 100 kHz magnetic field modulation. The samples, containing about 30 mg of substance in powder form, were placed into 4 mm diameter quartz tubes. The first derivatives of the power absorption spectra were recorded as a function of the applied magnetic field. The temperature dependence of the EPR spectra was investigated using an Oxford Instruments ESP helium-flow cryostat in the 3–300 K temperature range. The optimization of the spin Hamiltonian parameters and EPR data simulation was performed by using the software package EPR–NMR [13].

3. Results and discussion

Figure 2 presents (a) FIR and (b) MIR spectra of the Schiff base ligand 1T (upper panels) and the gadolinium Schiff base complex 1TGd (lower panels) at room temperature (RT).

The ν(C=N) vibration mode, in the Schiff base ligand, was observed at 1638 cm^{-1}. It confirmed the bicyclic condensation reaction occurrence with a consequent formation of the macrobicycle Schiff base. The ν(C=N) vibration mode moved to higher wavenumbers (by about 12 cm^{-1}) after complexation. The shift of the ν(C=N) stretching mode towards higher wavenumbers indicates a stronger double bond character of the iminic bonds and coordination of nitrogen of the azomethine group to the metal ion. Also the vibration of phenolic ν(OH) had moved from 3449 to 3419.8 cm^{-1} after complexation. The absorption band had shifted to lower frequencies, which indicates that the oxygen of the phenolic OH is coordinated to the metal ion. A band at 3419.8 cm^{-1} was observed for the complex; this indicates that there is another water molecule in the complex. The shifts of ν(O−H) and ν(C=N) are caused by the coordination of the oxygen atoms, which reduces the strengthening of the hydrogen bonds between the

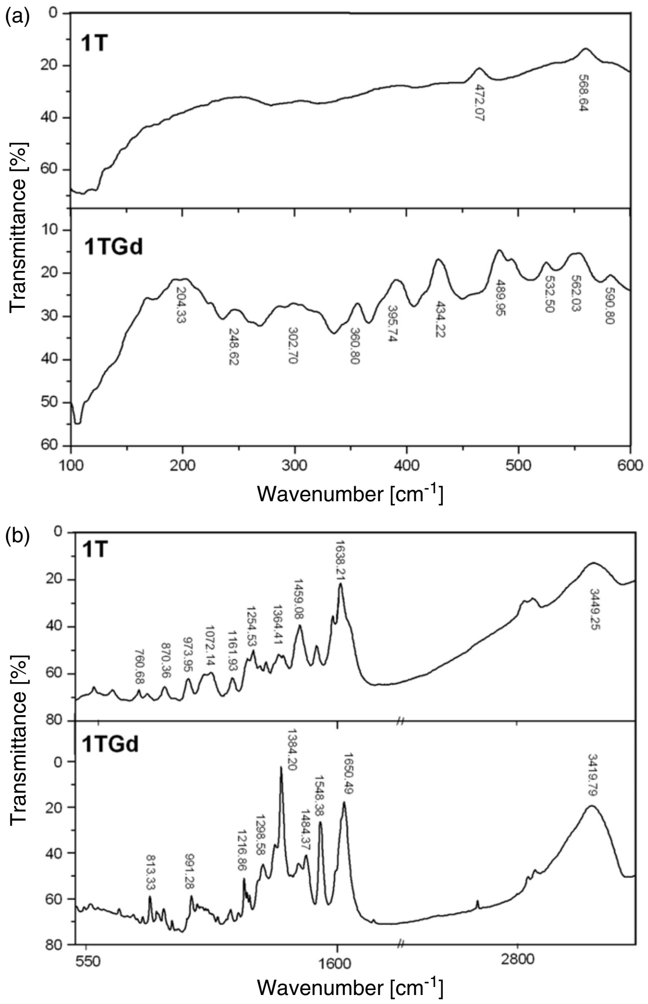

Figure 2. The FIR spectra (a) and (b) MIR spectra of the Schiff base ligand 1T (upper panels) and the gadolinium Schiff base complex 1TGd (lower panels) at RT.

ν(O–H) and ν(C=N) groups. The direction and magnitude of observed shifts of the bands associated with asymmetric nitrate vibrations is typical for bidentate ligands [17]. Besides, two wide bands assigned to M–N and M–O bonds were observed in the FIR spectrum of gadolinium cryptate at 395–489 and 532–590 cm^{-1}, respectively [14–19]. All bands characteristic for the Schiff base ligand and gadolinium cryptate are presented in table 1.

The TG-DTA analysis carried out up to 600 K revealed that there is a significant loss of mass of the sample at 520 K. The loss of mass analysis determined the presence of two water molecules in the inner coordination sphere of the metal ion. Thus the TG-DTA profile indicates the nine-fold coordination of the gadolinium ion.

Mass spectroscopy investigations gave evidences for the [1:1] monomeric nature of the gadolinium macrobicycle complex. Theoretically, for the [1:1] complex the molecular peak should have $m/e = 834$. In the electron spray spectrum of the 1TGd sample in this region a peak at $m/e = 832$ was obtained, indicating that during formation of the mentioned complex

Table 1. Characteristic absorption bands in both the Schiff base ligand and gadolinium cryptate complex.

Assignment	Schiff base ligand (cm^{-1})	Gadolinium cryptate (cm^{-1})
ν(M–N)		498.95
		434.22
		395.74
ν(M–O)		532.50
		562.03
		590.80
δ_{ring}	760.68	—
γ(C–H)	870.36	813.33
	973.95	991.28
ν(C–C)	1072.14	—
	1161.93	1216.86
δ(H–C=N)	1254.53	1298.58
ν(C–N)	1364.41	1359.21
δ_s(CH_2)	1459.08	1484.37
ν(C=C)	1600.09	1619.34
ν(C=N)	**1638.21**	**1650.40**
ν(CH_2)	2892.38	2899.67
ν(CH)	2917.92	2925.38
ν(OH)	**3449.25**	**3419.79**

three protons from a ligand were replaced by a gadolinium atom leading to a molecular peak at $m/e = 831$. The observed peak at $m/e = 832$ is the result of protonation of the sample. The molecular peak appearing in the mass spectrum as the isotope pattern is typical for a compound containing one gadolinium atom, confirming the [1:1] proportion of ligand and metal in the sample. Additionally, in the spectrum a peak at $m/e = 416$ was found. This peak was attributed to a double charged ion of the molecule.

Figure 3 presents the EPR powder spectra of the 1TGd complex at selected temperatures in the high-temperature range ($T > 160$ K) and in the low-temperature range ($T < 160$ K). The EPR signal consists of a main asymmetric, broad line with unresolved structure centred at $g \sim 2$ and many additional unresolved lines at lower ($g \sim 6$) and higher ($g \sim 1.5$) magnetic fields. The intensity of the spectrum varies considerably with temperature. The amplitude of the main peak at $g \sim 2$ decreases on lowering the temperature from 300 K down to 160 K and increases upon further cooling down to 3 K.

Gadolinium(III) ions are often used in paramagnetic complexes due to their good paramagnetism. The EPR spectra of gadolinium cryptates are similar to the EPR spectra of gadolinium in glasses. The characteristic feature is the presence of three lines centred at $g = 2$, 2.8 and 6, usually assigned to the weak, intermediate and strong crystal field, respectively. The EPR spectrum with three and more absorption signals is usually assigned to isolated Gd^{3+} ions, while a single broad absorption signal encompassing $g = 2$ is assigned to the clusters of Gd^{3+} ions [20–22]. Using computer simulation of the experimental EPR spectra arising from paramagnetic centres it is possible to extract the values of the spin Hamiltonian parameters required for the determination of structural information. For the Gd(III) ion with a 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) and S^2 (matrix D) as well as parameters associated with the high-spin terms of the type S^4 and S^6. For generation of the powder EPR spectrum the

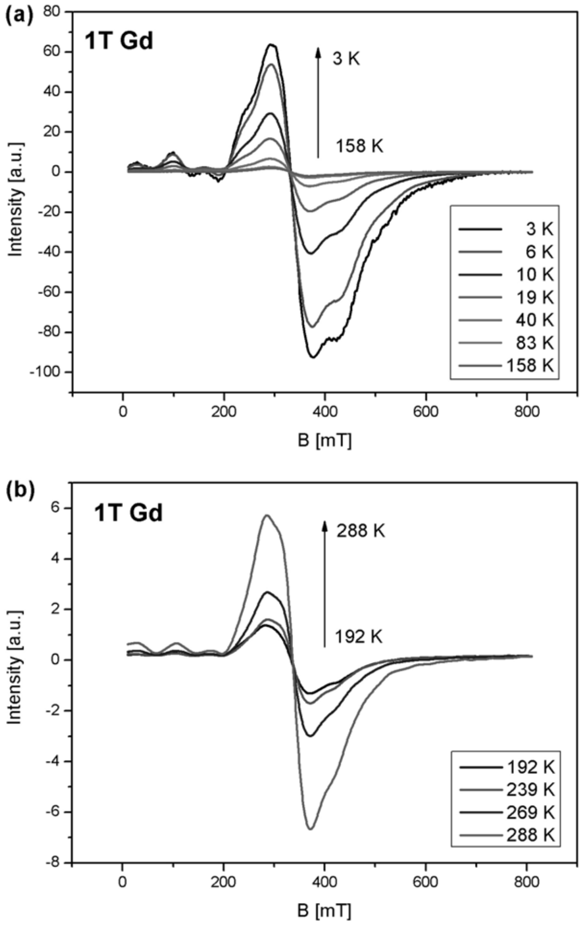

Figure 3. EPR spectra of the 1TGd complex at selected temperatures: (a) low-temperature range ($T < 160$ K); (b) high-temperature range ($T > 160$ K).

following spin Hamiltonian was used:

$$H_s = \mu_B S \cdot g \cdot B + S \cdot D \cdot S + \sum_{m=-l}^{l} B_l^m \cdot O_l^m(S), \tag{1}$$

where the first term is the electronic Zeeman term, the second represents the fine structure electronic quadrupole term and the third contains terms of degrees S^4 and S^6 in Stevens notation. In equation (1), μ_B is the Bohr magneton, B is the applied magnetic field, $O_l^m(S)$ are Stevens operators of degree m, and B_l^m are Stevens parameters [23]. The number of parameters different from zero B_l^m depends on the site symmetry of the paramagnetic centre.

All registered EPR spectra of the investigated complex at different temperatures have been simulated using the EPR–NMR computer program in order to study the thermal changes of the spin Hamiltonian parameters. As an example, figure 4 presents experimental (upper panel) and simulated (middle panel) spectra of the 1TGd complex at 4.75 K. The accordance between these two spectra is satisfactory, as can be seen in the lower panel in figure 4, which shows their difference, with no apparent structure visible. Similar acceptable fittings were obtained for the

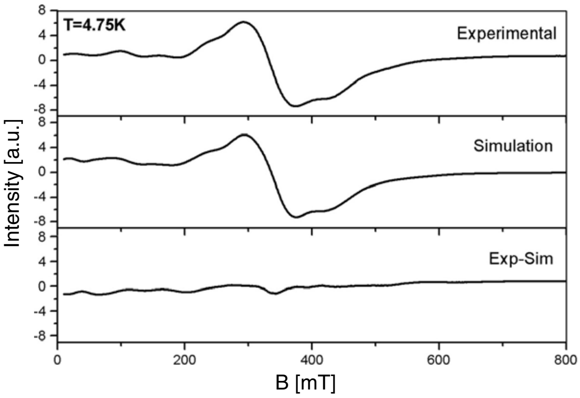

Figure 4. Experimental (top panel), simulated (middle panel) and the difference (lower panel) of the EPR spectra of the 1TGd complex at $T = 4.75$ K.

Table 2. Calculated values of the spin Hamiltonian parameters for the 1TGd complex at 4 K.

		Stevens parameters in units of Gs			
g tensor	D tensor (Gs)	m	$B(4; m)$	m	$B(6; m)$
$g_{xx} = 2.07$	$D_{xx} = 93$	0	1.1	0	−0.025
$g_{yy} = 2.02$	$D_{yy} = 114$	1	1.8	1	−0.450
$g_{zz} = 2.05$	$D_{zz} = -236$	2	0.0	2	−0.250
		3	9.0	3	0.650
		4	3.6	4	0.000
		−4	0.0	5	0.000
		−3	−6.0	6	0.000
		−2	0.0	−6	0.000
		−1	−3.5	−5	0.050
				−4	0.000
				−3	−0.300
				−2	−0.080
				−1	0.460

EPR spectra at other temperatures. In table 2, as an example, the calculated spin Hamiltonian parameters for $T = 4.75$ K are given. The presence of three different g_i and D_i $(i = 1, 2, 3)$ components and non-zero values of many B_l^m parameters (for $l = 4, 6$) indicates the low symmetry of the crystal field at the Gd(III) site. The accuracy of the calculated parameters has been estimated by varying the values of the parameters and observing the 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 entirely reliable (similarly as in case of other methods used for powders 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 0.5 Gs for the B_4^4 parameter and 0.03 Gs for B_6^{-1}, B_6^{-2}, B_6^1 parameters.

Analysis of the thermal dependence of the spin Hamiltonian parameters showed that g_i and D_i do not change with temperature, while many B_l^m $(l = 4, 6)$ parameters displayed significant temperature dependence. Two temperature ranges can be recognized in which the calculated

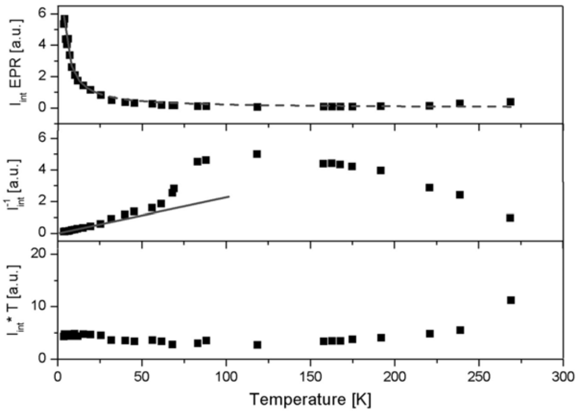

Figure 5. Temperature dependence of the EPR integrated intensity for the 1TGd complex (upper panel), of the reciprocal integrated intensity (middle panel), and the product TI_{int} (lower panel).

spin Hamiltonian parameters B_l^m ($l = 4, 6$) showed significant changes: the high-temperature range, $T > 160$ K and the low-temperature range, $T < 30$ K. In the low-temperature range the values of B_4^4 and B_6^{-2} decreased about 30%, and B_6^{-1} and B_6^1 increased by 30% with temperature increase from 3 to 30 K. In the high-temperature range the parameters B_4^{-4}, B_4^{-2}, B_4^2, which had zero values below 160 K, acquired non-zero values. At RT the values of these parameters were $B_4^{-4} = 3.5$ (Gs), $B_4^{-2} = 1.0$ (Gs), $B_4^2 = -1.0$ (Gs), while the B_6^3 parameter value decreased from 0.65 Gs at 160 K to zero at RT. In the temperature range 30–160 K the values of all parameters were observed to be constant.

An important spectroscopic parameter that can be calculated from the EPR spectrum is the integrated intensity I_{int}. It is defined as the area under the absorption resonance line (not the usually registered first derivative of this line) and is proportional to the imaginary part of the complex magnetic susceptibility of the investigated spin system. Study of the temperature dependence of I_{int} could reveal the magnetic interactions between spin species. Figure 5 displays the results of the temperature studies of I_{int} for the 1TGd complex. The upper panel in figure 5 presents the temperature dependence of I_{int}, the middle panel the reciprocal integrated intensity I_{int}^{-1}, and the lower panel the product of temperature and integrated intensity, $T \cdot I_{\mathrm{int}}$. Inspection of figure 5 shows that there is no magnetically ordered state in this compound down to a temperature of 3 K. As the temperature decreases from RT, I_{int} decreases slightly down to $\sim$130 K, and on further cooling starts to increase at accelerated rate at low temperatures. It is clear that the thermal changes of I_{int} could not be described by a simple Curie–Weiss relation, $I_{\mathrm{int}} = C/(T - \theta)$, in the whole temperature range investigated. In the low-temperature range, 3–25 K, there is a linear dependence of I_{int}^{-1} (figure 5, middle panel), and in that range the Curie–Weiss relation holds, with practically zero value of the Curie–Weiss constant $\theta = -0.42(39)$ K. It follows that there are no magnetic interactions between 1TGd complexes below 25 K. On the other hand, in the high-temperature range, $T > 160$ K, the situation is quite different. As the product TI_{int} is proportional to the square of the effective magnetic moment, the lower panel in figure 5 indicates that the magnetic moment decreases appreciably as the temperature is lowered from RT. If this decrease is due to gadolinium ions at high temperatures there is a significant antiferromagnetic interaction between the Gd(III) complexes. This interaction between neighbouring complexes might favour the formation of a certain number of short-lived (on the timescale of the EPR spectroscopy, $\tau \sim 10^{-10}$ s) dimers with a 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. Investigation of a static magnetic susceptibility by dc magnetization measurements might not account for that contribution from the dimers. Another possible explanation of the temperature behaviour of the effective magnetic moment is the existence of other paramagnetic centres, such as uncontrolled dopant presence in the sample investigated. But this possibility seems not very probable as the mass spectroscopy investigation did not confirm the presence of another admixture and there are no EPR lines arising from such centres.

The lowering of the effective magnetic moment of the Gd(III) complex in the high-temperature range correlates with the changes in values of many B_l^m ($l = 4, 6$) parameters. Thus magnetic interaction between neighbouring complexes leading to temporal formation of dimers could deform the complex slightly, changing the values of certain B_l^m ($l = 4, 6$) parameters. In the low-temperature range slight changes in certain B_l^m ($l = 4, 6$) parameters could not be connected with the magnetic interaction between complexes because there is no such interaction, as evidenced by a near zero value of the Curie–Weiss constant.

4. Conclusions

IR measurements have evidenced the formation of the 1TGd complex, in which the nearest neighbourhood of Gd(III) consists of nine ions: five oxygens and four nitrogens. The local symmetry at the Gd(III) site is low, as proved by the presence of many non-zero parameters in the spin Hamiltonian. The temperature dependence of the EPR integrated intensity indicates that there is no magnetically ordered state in this compound down to a temperature of 3 K. In the high-temperature range, $T > 160$ K, strong antiferromagnetic interactions between Gd(III) complexes are evidenced by decreasing magnetic moment as the temperature decreases. This interaction might favour formation of the short-lived dimers with a non-magnetic ground state.

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