FT-IR, ESI and EPR studies of a Dy(III) Schiff base podand complex

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ABSTRACT

IR spectroscopic, electrospray ionization mass spectrometry, structure and magnetic properties of a dysprosium(III) macrocyclic tripodal Schiff base tris((2-(5-chlorosalicylideno)amino)ethyl)amine (*tren-5Clsal*) complex are reported. The positions of v(C=N) stretching bonds indicate that the azomethine group nitrogen is coordinated to the rare earth ion. Two main spectral components are observed in the low magnetic field region (<300 mT) in the EPR spectra, independently of temperature. These components are attributed to the Dy^{3+} ion with an effective spin of $S = 1/2$. The magnetic anisotropy between 3 and 23 K is practically constant as evidenced only by a marginal change of the spread of g-factors. The g_y-factor increases strongly with an increase in temperature above 23 K, giving rise to a very high magnetic anisotropy of the complex. Such behavior of the magnetic anisotropy at a higher temperature could be an effect of the existence of an excited doublet. A very small value of the Curie–Weiss constant and the lack of any meaningful thermal changes of linewidths indicates the absence of any significant interactions between Dy(III) complexes below 20 K. The temperature dependence of the total integrated intensity above 20 K indicates the existence of an excited doublet, occurring about 33(1) K above the ground state.

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1. Introduction

The application of lanthanide(III) ions in molecular chemistry has been a very active field of research recently. These ions can be used when designing novel probes of biomedical interest [1] and when preparing new kinds of catalysts and enzymes [2–4]. Their high magnetic moments, along with their magnetic anisotropy are of particular interest in the field of molecular magnetism. The magnetic studies have been mostly limited to the case where the lanthanide(III) ion is Gd(III). In fact, the pure spin ground state of gadolinium has permitted a simple analysis of the magnetic properties using the spin Hamiltonian. The Gd(III) interaction has been found to be of a ferromagnetic type in [1 + 1] Schiff base podates [3] and in some other investigated compounds with gadolinium [4,5].

The formation of mononuclear Schiff base podates has been achieved with d- and f-transition ions. In recent years, considerable attention has been devoted to [1 + 1], [2 + 1], [1 + 2] or [3 + 1] podates derived from a template condensation of appropriate amine-precursors in the presence of lanthanide(III) salts. Special attention has been attracted by pendant arm podands and their

complexes [6–14]. Arms bearing additional potential of ligaturing groups have been introduced at both carbon and nitrogen atoms of macrocycles. The interesting properties may arise from their high flexibility. Their cyclic and acyclic nature has been confirmed especially by IR, NMR spectroscopy and mass spectrometry. It has been also clearly indicated by a single crystal X-ray structural study.

In one of our previous papers we have presented the EPR properties of a gadolinium Schiff base podate (LnL = (Ln=Gd, L = tripodal heptadentate N_4O_3 tris[(2-(5-chlorosalicylidene)amino)-ethyl]amine (*tren-5Clsal*): $C_{27}H_{27}N_4O_3Cl_3Gd$, designated as 33TGd) [5]. We have confirmed [1:1] the complex form and we have investigated its spectroscopic and magnetic properties. A new Schiff base podand complex with another paramagnetic ion – dysprosium(III) with the formula $C_{27}H_{27}N_4O_3Cl_3Dy$ is presented in this paper as a continuation of that study. In the previous paper [5] the ligand is designated as 33T ($C_{27}H_{27}N_4O_3Cl_3$). Dysprosium exhibits characteristic transitions leading to blue (485 nm) and yellow (575 nm) emissions.

Kanesato and Yokoyama have previously reported similar but not identical crystal structures of $LnL^1 =$ (Ln=Dy, Ho, $L^1 =$ tris((2-(salicylidene)amino)ethyl)amine) with the formula $C_{27}H_{27}N_4O_3Dy$ [7]. They have found that individual metal ions

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and apical nitrogen atoms lie on a 3-fold axis and the molecule has a C_3 molecular symmetry.

In the present paper we report on the structure, spectroscopic and magnetic properties of Dy(tren-5Clsal) (33TDy) powder samples. These properties have been investigated using MM3 mechanics calculations, Infra-Red (IR), electrospray ionization mass spectrometry (ESI MS), and Electron Paramagnetic Resonance (EPR) techniques.

2. Experimental

The synthesis of a dysprosium Schiff base podate was carried out according to a known method described for the first time by Malek et al. [15].

The FT-IR spectrum of Dy(tren-5Clsal) was recorded in nujol and fluorolube with an IFS 113v FT-IR spectrophotometer (Bruker, Karlsruhe) equipped with a DTGS detector; resolution 2 cm^{-1}, NSS = 125. The Happ-Genzel apodization function was used. All manipulations with the substances were performed in a carefully dried and CO_2-free glove box.

The ESI mass spectra were recorded on a Waters/Micromass (Manchester, UK) ZQ mass spectrometer equipped with a Harvard Apparatus syringe pump. All samples were prepared in methanol. The measurements were taken for samples being a solution of Dy(tren-5Clsal) (5×10^{-5} mol dm^{-3}). The sample was infused into an ESI source using a Harvard pump at a flow rate of 20 µl min^{-1}. The ESI source potentials were: capillary 3 kV, lens 0.5 kV, extractor 4 V. The standard ESI mass spectra were recorded at the cone voltages of 10, 30, 50, 70, 90 and 110 V. The source temperature was 393 K and the dissolvation temperature was 573 K. Nitrogen was used as the nebulizing and dissolvation gas at the flow-rates of 100 and 300 dm^3 h^{-1}, respectively. Mass spectra were acquired in the positive ion detection mode with the unit mass resolution with a step size of 1 m/z unit. The mass range for ESI experiments was changed from m/z = 100 to m/z = 1000.

The structure of the [tren-5-Clsal + Dy + H]$^+$ ion was calculated by the MM3 molecular mechanics method (using Win Mopac 2007).

The EPR spectra were recorded on a conventional X-band Bruker ELEXSYS E 500 CW-spectrometer operating at 9.5 GHz with 100 kHz magnetic field modulation. The investigated samples had a fine powder form. The first derivative of the power absorption spectra was recorded as a function of the applied magnetic field. The temperature dependence of the EPR spectra in the 3–300 K temperature range was recorded using an Oxford Instruments ESP helium-flow cryostat. The optimization of spin-Hamiltonian parameters and the EPR data simulation were accomplished using the SIMPOW [7] software package in the temperature range of 3–55 K. A weak signal and large noise observed at high temperatures permitted a reliable simulation of experimental data above 70 K.

3. Results and discussion

3.1. IR spectroscopy

The tren-5Clsal FT-IR spectra (dashed line) and its 1:1 complex with a Dy^{3+} cation (solid line) are compared in Fig. 1(a). A broad band in the region of 3000–2000 cm^{-1} with a maximum at about 2650 cm^{-1} occurs in the tren-5Clsal spectrum. This band is assigned to hydrogen vibrations within intramolecular O-H···N hydrogen bonds [16]. No absorption characteristics for v(OH) vibrations indicating that all phenolic groups are deprotonated and that they are involved in a complexation process are observed in the spectrum of the complex. Furthermore, the spectrum indi-
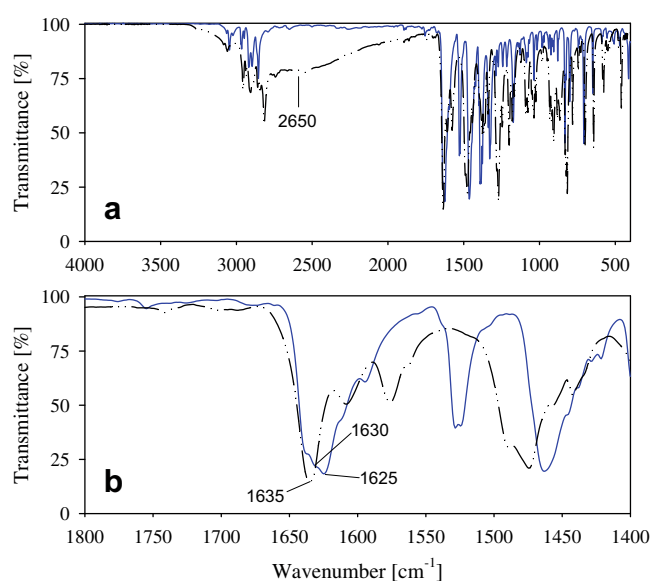

Fig. 1. FT-IR spectra of tren-5Clsal (dashed line) and its complex with Dy^{3+} (solid line) in nujol and fluorolube in the regions: (a) 4000–400 cm^{-1}, (b) 1800–1400 cm^{-1}.

cates that no water molecules are present in the metal cation's coordination sphere, either.

A few bands are assigned to the v(C=C) of aromatic rings in the spectrum of the ligand in the region 1650–1550 cm^{-1}. Moreover, a relatively intense and sharp band assigned to v(C=N) vibrations is found at 1635 cm^{-1} (see Fig. 1(a)) [16,17]. This band becomes broadened and complex in the spectrum of complexes showing three maxima at 1635, 1630 and 1625 cm^{-1} (Fig. 1(b)). This spectral feature demonstrates a different involvement of the nitrogen atoms of the imine groups in the coordination process of the Dy^{3+} cation. The deprotonation of the OH groups has also an impact on the strong shifts of the respective positions of the bands assigned to the v(C=C) vibrations. They arise in the region 1610–1450 cm^{-1}, due to the strong changes of the electron density distribution in the aromatic system after the Dy^{3+} cation complexation.

3.2. ESI MS studies

The ESI spectra and the main m/z signals measured at various Dy(tren-5Clsal) cone voltages are given in Fig. 2. One signal at $m/$
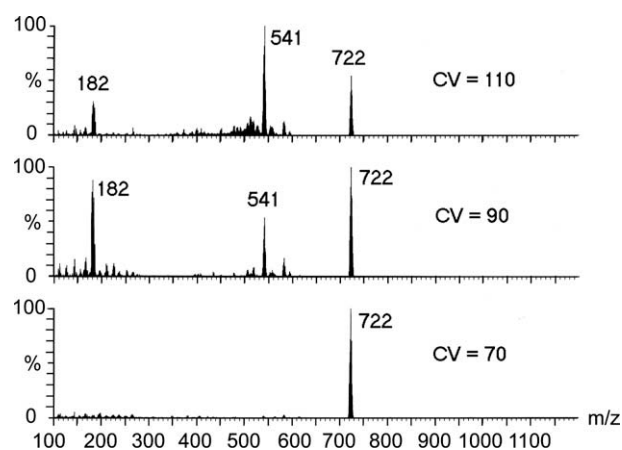

Fig. 2. ESI MS spectra of a 1:1 tren-5Clsal-Dy^{3+} complex dissolved in methanol recorded at various cone voltage values of 70–110 V.

$z = 722$ is observed in the ESI spectrum of this complex in the range of $cv = 10$–70 V corresponding to the mono-protonated 1:1 Dy(t-ren-5Clsal). This signal is observed still at $cv = 90$ V and new medium relative intensity signals appear at $m/z = 541$ and $m/z = 182$. These signals can be assigned to fragmentary ions whose structures are shown in Fig. 3. The intensity of the peaks, corresponding to the fragmentary ions, could serve as evidence of a mild fragmentation. The signal at $m/z = 541$ becomes main in the ESI MS spectrum at $cv = 110$ V with the increasing cone voltage values. A comparison of the isotopic distribution observed in the spectrum with the calculated distribution for the signal at $m/z = 722$, shown in Fig. 4, has confirmed the presence of monoprotonated Dy(tren-5Clsal). The protonation occurs probably on a tertiary N amine atom. The proposed calculated structure of this complex [tren-5Clsal + Dy + H]$^+$ is shown in Fig. 5.

3.3. EPR spetroscopy

A Dy(III) ion has a 4f^{9+} electronic configuration of a $^6H_{15/2}$ free-ion ground state. The 16-fold ground state degeneracy is split by a crystal field and eight Kramers doublets are formed in case of trigonal or tetragonal symmetry. The lowest doublet may be Γ_6 (with theoretically predicted $g = 6.67$) or Γ_7 (with $g = 7.56$). It is often assumed that Dy(III) could be approximated by an effective spin $S_{eff} = 1/2$ with anisotropic g values. This is possible since the Ising-like behavior is frequently exhibited by Dy(III)-containing compounds. EPR studies have shown that the values of $g_\perp$ are in general very small with respect to those of $g_\parallel$ which are very large. This anisotropy of g-factors makes it possible to treat Dy(III)-compounds as an Ising system at low temperatures [8–11]. The literature on EPR investigations of dysprosium organometallic complexes is scarce. The magnetic properties and structure of a Cu(II)Dy(III) heterodinuclear Schiff base complex have been investigated and discussed in Ref. [18]. The magnetic properties of the compound are dominated by a crystal field effect on the Dy(III) site, masking the magnetic interaction between the paramagnetic centers. It has been noticed that a parallel alignment of Cu(II) and Ln(III) spin moments for 4f^8–4f^{13} configurations would result in an overall ferromagnetic interaction.

Fig. 6 shows selected Dy(tren-5Clsal) EPR spectra taken at four different temperatures: 3.9, 6.14, 13.3 and 27.1 K. Two main spectral components in a low magnetic field region (<300 mT) are observed for all investigated temperatures. They were attributed to Dy^{3+} ions with an effective spin $S = 1/2$. The intensity of both spectral components increases significantly with a decrease in temperature. The registered EPR spectra were simulated by the SIMPOW computer program to extract relevant spectral parameters. The simulated spectra were reasonably close to the experimental ones, although a weak but persistent shoulder was not reproduced by the simulation at about 280 mT. Fig. 7 presents, as an example, the simulated and experimental spectra obtained at 3.5 K for two
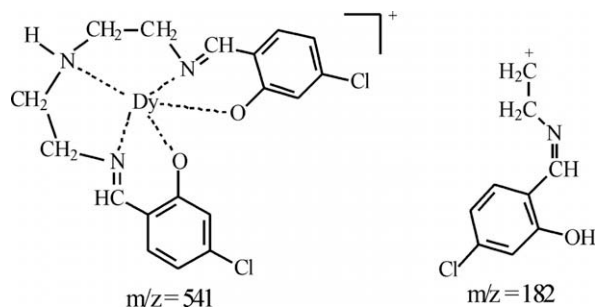

Fig. 3. Proposed structures of main fragmentary ions detected in ESI MS spectra at high cone voltage values.
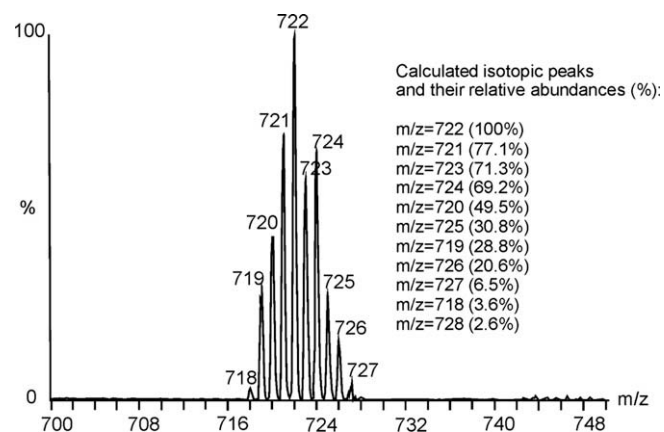

Fig. 4. Calculated isotopic peaks and their relative abundances of the [tren-5Clsal + Dy + H]$^+$ signal at $m/z = 772$ compared with that obtained experimentally from the ESI MS spectrum.

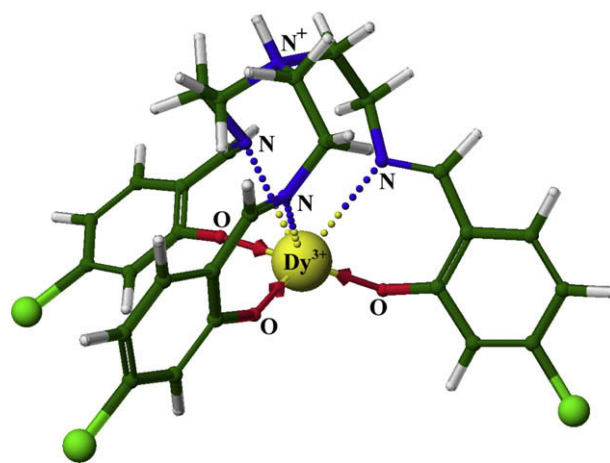**Fig. 5.** The structure of a [tren-5Clsal + Dy + H]$^+$ ion detected in the ESI MS spectra at $m/z = 772$, calculated by the molecular mechanics method (MM3 method, Win Mopac 2007).
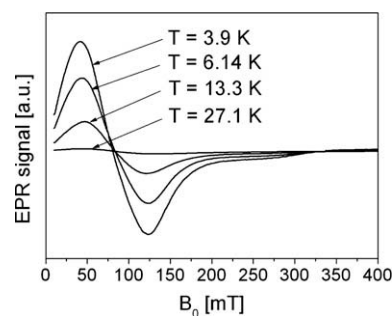
Fig. 6. Representative Dy(tren-5Clsal) EPR spectra registered at different temperatures.

possible symmetries of paramagnetic centers: orthorhombic ($g_x \neq g_y \neq g_z$) and axial ($g_x = g_y \neq g_z$). As can be seen in Fig. 7, axial symmetry of the paramagnetic center (see [7]) is less probable than orthorhombic symmetry (better fitting is observed at low magnetic fields). The following effective spin Hamiltonian for an effective spin $S = 1/2$ has been applied,

$$H = \beta B \cdot g \cdot S, \tag{1}$$

Fig. 7. Comparison of an experimental and simulated Dy ion spectrum at 3.5 K.

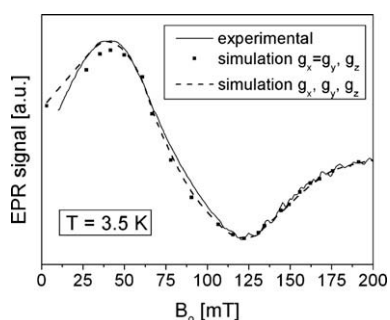**Fig. 8.** Temperature dependence of the calculated anisotropic g_i-factors (upper panel) and anisotropic linewidths ΔB_i (lower panel).

Table 1
Values of the calculated principal g_i-factors and an average g-factor at 3.5 and 52 K

Temperature (K)	g_x	g_y	g_z	g_{av}
3.5	8.05	14.55	5.69	9.43
52	3.00	31.93	7.89	14.27

where all symbols have their usual meaning. The calculated values of the three principal g_i-factors and an average g-factor (defined as $g = (g_x + g_y + g_z)/3$) at the lowest registered temperature of 3.5 K and at a rather high temperature of 52 K are listed in Table 1. The g-values and anisotropic linewidths, ΔB_i, were determined by solving the least-squares problem and making a comparison of the calculated values to a complete set of measured values in the SIMPOW program. Fig. 8 shows the temperature dependence of the obtained anisotropic g_i-values (upper panel) and the anisotropic linewidths, ΔB_i (lower panel).

The temperature dependence of the spin Hamiltonian parameters has revealed the presence of two different temperature regions. The linewidth and the g_x, g_z factors in the 3–18 K temperature range remain almost constant and only small changes of the g_y factor are evident. A strong change of linewidths observed at the lowest temperature (Fig. 8) might be a sign of critical slowing down of spin correlations connected with an approach to a magnetic ordered phase, however, since experimental evidence of such transition is lacking it will not be discussed further. A strong increase in g_y-factor, ΔB_y and ΔB_z linewidths is observed above 23 K. It should be noticed that the g_x and g_z factors cross over close to this temperature. The magnetic anisotropy between 3 and 23 K is practically constant as evidenced by only a marginal change of the g-factors spread, while the g_y factor increases strongly above 23 K with the increasing temperature, which gives rise to a very high magnetic anisotropy of the complex at high temperatures. Although the obtained values of spectral parameters in that temperature range are less reliable than below 20 K (due to a small intensity of the EPR signal) the overall observed tendency is to be trusted. This impressive change of magnetic anisotropy and EPR lines broadening could be only an apparent change due to the superposition of lines arising from the ground and the excited doublets and will be discussed further.

The integrated EPR intensity I_{int} is an important spectroscopic parameter that can be calculated from the EPR spectrum. It is defined as the area under the absorption resonance line and is proportional to the imaginary part of the complex magnetic susceptibility of the investigated spin system. Should the temperature dependence of I_{int} be studied, magnetic interactions between spin species could be revealed. Fig. 9 displays the results of the temperature studies of I_{int} for the Dy(tren-5Clsal). The upper panel in Fig. 9 presents the temperature dependence of I_{int}, the middle panel – the reciprocal integrated intensity I_{int}^{-1} (in low and high temperature ranges with a different scale of reciprocal integrated
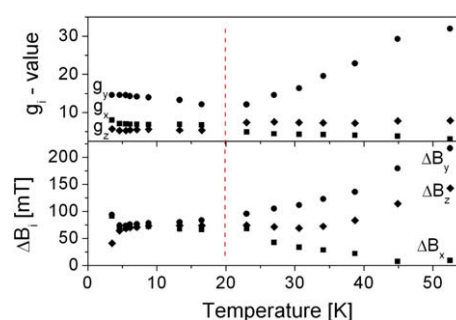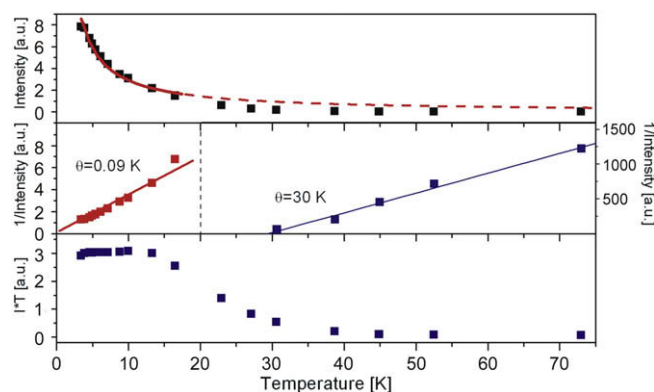

Fig. 9. Temperature dependence of the integrated intensity I_{int} (upper panel), reciprocal integrated intensity I_{int}^{-1} (middle panel; left hand side – in a low temperature range, $T = 3$–20 K, right hand side – in high a temperature range, $T = 20$–75 K; (please note a different scale of the reciprocal integrated intensity), and the product $T \cdot I_{int}$ (lower panel).

intensity), and the lower panel – the product of the temperature and the integrated intensity, $T \cdot I_{int}$.

There is a linear dependence of I_{int}^{-1} (Fig. 9, middle panel, left hand side) in the low temperature range from 3 to 20 K, and the Curie–Weiss relation holds in that range, with the value of the Curie–Weiss constant, $\theta = 0.09(7)$ K, being practically zero. A very small Curie–Weiss constant value and the lack of any significant thermal changes of the linewidths indicates the absence of any major interaction between Dy(III) complexes below 20 K. An approximation of the low-temperature Curie–Weiss curve to the high-temperature range ($T > 20$ K) shows that the observed spin susceptibility is lower than expected for a system of non-interacting spins. Apparently, a part of the spin system is arising from the excited doublet. The difference, ΔI_{int}, between I_{int}^{CW}, calculated from the low-temperature Curie–Weiss law and $I_{int}^{obs.}$, observed in exper-
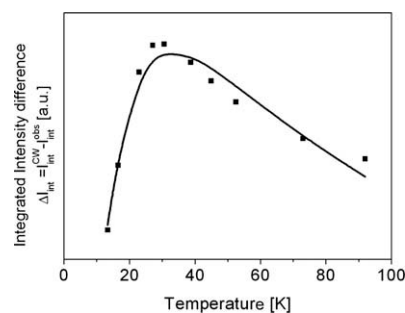

Fig. 10. Thermal dependence of the integrated intensity difference, $\Delta I_{int} = I_{int}^{CW} - I_{int}^{obs.}$, (full squares). The solid line is the least square fitting to the function (2) with $T_0 = 33(1)$ K.

iment is presented in Fig. 10. The number of spins in the excited state increases as the temperature rises from 20 K, and, reaches a maximum at about 30 K. The temperature dependence of ΔI_{int} suggests that the resonance spectrum reflects the existence of an excited state. It could be analyzed in terms of the following equation:

$$I(T) = \frac{\alpha}{T} \cdot \exp\left(-\frac{T_0}{T}\right), \tag{2}$$

where T_0 is the energy difference (expressed in K) between the ground state and the excited state. The fitting of Eq. (2) to the experimental points shows that the excited state is about 33(1) K above the ground state.

Fig. 9(b) indicates that the spins interact ferromagnetically in the temperature range above 30 K and are characterized by the Curie–Weiss constant of $\theta = 30$ K. The apparent deviation from simple Curie type intensity behavior can be most easily modeled by assuming a thermal population of next higher Kramers doublets. Such a process would be intra-molecular without requiring an assumption of inter-molecular interactions. An assumption of a ferromagnetic interaction between the excited doublets and a depopulation of these doublets below ∼20 K seems to be the only consistent way of explaining the observed thermal behavior of g-factors and the lack of a long-range magnetic order in this material. It should also be noted that the derived average g values are way off from the expected values and this fact could be only explained by the influence of higher Kramers doublets. In Ref. [19] three broad signals in the magnetic field range from 400 to 1500 G have been registered and assigned to Dy^{3+} ions in the EPR spectrum of a non-oriented sample of $Dy_{0.01}Y_{0.99}Ba_2Cu_3O_x$. The temperature dependence of the intensity of one of the lines follows the Curie-law, whereas the intensity of the other two resonance values increases with an increase in temperature. This behavior would suggest that the former resonance results from the ground state and the latter lines originate from the first excited state of the Dy^{3+} ion. It has been concluded that the resonance field of the first line corresponds to $g_{\parallel}$ of the ground state doublet, and the other two lines correspond to the $g_{\parallel}$ and $g_{\perp}$ values of the excited doublet. Our powder EPR spectrum of Dy^{3+} in Dy(trans-5Clsal) is a superposition of both spectra from the excited and ground doublets. Therefore, the observed thermal change of g-factors and linewidths at ∼20 K could be interpreted as a result of thermal depopulation of the excited doublets below that temperature.

It is impossible to identify the ground and excited states of bulk paramagnetic complexes and antiferromagnetically coupled pairs at this stage of investigation as the structure of the complex is very complicated. As the crystal field parameters of a Dy^{3+} ion in a Dy(t-ren-5Clsal) complex have not been determined yet, any calculation of theoretical g-factors and their comparison with experimental values is not possible at this moment. Growing of a single crystal and its subsequent investigation by the EPR technique would be re-

quired to determine detailed magnetic anisotropy to get a deeper insight into the magnetic structure of Dy(tren-5Clsal).

4. Conclusions

A v(C=N) stretching bond has been observed in Dy(tren-5Clsal) powder samples in the FIR spectrum as shifted towards a lower energy region at $1625\ cm^{-1}$ which indicates that the azomethine group nitrogen is coordinated to the rare earth ion. No bands characteristic for the v(OH) vibrations have been found in the FIR spectrum which would indicate that all phenolic groups are deprotonated without being involved in the complexation process. It also indicates that no water molecules are present in the coordination sphere of the metal cation. Furthermore, two wide bands assigned to M–N and M–O bonds have been observed. The thermal dependence of the g-factor is evidence of an increasing magnetic anisotropy of the complex with the increasing temperature. The EPR signal in the high temperature range ($T > 20$ K) of Dy(tren-5Clsal) originates from the paramagnetic, non-interacting spins which is evidenced by the integrated intensity following the Curie law. The observed deviation from the Curie type behavior of integrated intensity, characterized by the Curie–Weiss constant $\theta = 30$ K, could be explained by the influence of the excited Kramers doublet. The temperature dependence of the integrated intensity suggests the existence of an excited state, occurring about 33(1) K above the ground state.

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