Spectral and magnetic properties of macroacyclic and macrobicyclic Schiff base RE complexes

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ABSTRACT

IR spectroscopic, electrospray ionization mass spectrometry, TG-DTA, structure and magnetic properties of the gadolinium(III), samarium(III) and dysprosium(III) macroacyclic tripodal Schiff base, $C_{27}H_{27}N_4O_3C_{13}Gd(Dy, Sm)$ as well as gadolinium(III) and erbium(III) cryptate $C_{39}H_{47}MN_9O_6$ (M=Gd, Er) complexes are reported. The positions of $\nu(C=N)$ stretching bonds indicate that the azomethine group nitrogen is coordinated to the rare earth ion. The [1:1] ligand to metal proportion in all macrocyclic and mocrobicyclic Schiff base complex samples has been confirmed by both electron ionization and electron spray molecular spectroscopy spectra. A TG-DTA analysis has indicated the presence of two water molecules in the inner-sphere of the macrobicyclic complex and confirmed that there is no water coordination of the metal ion in the macroacyclic complex. The near neighborhood of cation ions in the complexes of both types and their structure have been proposed on the basis of the above data. The temperature dependence of the EPR spectra integrated intensity has made it possible to reveal magnetic interactions in the spin system of these compounds.

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1. Introduction

Macrocyclic compounds are interesting because of their ability to form complexes with transition metal ions and rare-earths (RE). Over the last decade, sustained research activity devoted to lanthanide ions and their macrocyclic and macrobicyclic complexes has to some extent resulted from successful applications of these compounds in the industry, medicine and biology. Such macroacyclic compounds as podands have a higher flexibility of arms and their complexation ability grows with the ionic radius of rare-earth ions. The formation of macrobicycle compounds (such as cryptates) depends to a large extent on the accuracy of the cation fit in the ligand cavity. They are more rigid than macroacyclic compounds. Lanthanide ions can be used in the design of novel fluorescent probes, luminescence labels (detecting small amounts of biomolecules that can provide information about the patient's physical condition) of biomedical interest [1]. Macrocyclic complexes based on RE ions can imitate the complicated structure of an enzyme, they are however significantly smaller and simpler. They are applied to cure leukemia, they have antivirus activity (Oxphaman), they are used in medical diagnostics, treatment of arteriosclerosis, radioimmunology, as the contrast medium, as a synthetic enzyme to split a nucleic acid chain [2–4]. They reveal bactericidal, mycosicidal and nailicidal properties.

They can be also applied in preparation of new kinds of catalysts and enzymes [5]. The metal ion in macrocyclic compounds locates itself inside a cavity formed by rings and aliphatic arms. Hence, the compounds are used in chemical analysis and synthesis to fix an aminoacid composition, to detect finger traces, to separate selected metals and supramolecular devices. Macrobicyclic ligands can find potential application in selective extraction of metals.

Moreover, they can find extensive application in optoelectronics as photoluminescence materials, as nonlinear optical materials (e.g. N-(R-salicylideno)-R′-anilin), as reversive optical storage, solar filters, photostabilizers, dyes for solar collectors, molecular switches (due to the photochromic properties) [6].

Schiff bases are macroacyclic (MaSB) or macrobicyclic (MSB) compounds with an imine group. The general formula of a Schiff base is R-CH=N-R′. The chemical and physical properties of the compounds strongly depend on the R and R′ substituents. The complexes of both types are built of one (two) nitrogen atoms that hold three ligand arms with an azometine group (Schiff base) in each of them, two aliphatic arms (CH_2), one aromatic ring connected with chlorine (methyl) on the opposite site and a phenolic group. The OH phenolic groups within the complex are involved in intramolecular hydrogen bonds with the respective nitrogen atoms of the Schiff base. When a complex is formed the bonds are broken and a metal cation ion is adjoined. Macrocyclic and macrobicyclic compounds have been designed to form [1:1], [1:2] and more metal ion complexes.

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On the basis of the performed measurements, we have proposed in this paper a structure of macrobicycle Schiff base complexes with gadolinium and erbium as well as macroacycle Schiff base complexes with gadolinium, dysprosium and samarium, giving also the distances from the RE ion to the closest neighboring ions. The presented results are characteristic and recurrent for other RE ions in the above mentioned complexes. The paper is aimed as a mini-review, although semiempirical calculations of structures of the above mentioned complexes are presented for the first time.

2. Experimental

A synthesis of macroacyclic (MaSB) and macrobicyclic (MSB) complexes was carried out by condensation of appropriate amine-precursors in the presence of lanthanide (III) salts whose cation is assumed to act as a ring formation template.

A synthesis of gadolinium and dysprosium Schiff base podates, $C_{27}H_{27}N_4O_3Cl_3M$ (M=Gd, Dy) was made using the known methods described for the first time by Liu et al. [7] and Malek et al. [8], respectively.

A synthesis of gadolinium and erbium macrobicyclic cryptate complexes, $C_{39}H_{47}MN_9O_6$ (M=Gd, Er), was performed according to [9,10].

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 MaSB and MSB complex powder mixed with KBr and pressed into pellets and complex powder immersed in oil and placed between CaF$_2$ plates. The Schiff base ligand and gadolinium complex spectra were recorded at room temperature (RT) with the resolution of 2 cm^{-1}.

A mass spectroscopy analysis was performed using the following devices: the electron ionization (EI) mass spectrum of the measured samples was registered using the AMD 604 system (EI 70 eV, Temp = 346 K); the Mariner of PE Biosystems spectrometer operating with a TOF detection system was used for the electron spray (ES) mass spectrum (MeOH solution, positive ions, NP = 400). The ESI mass spectra were recorded on a waters/micromass (Manchester, UK) ZQ mass spectrometer equipped with a Harvard Apparatus syringe pump. The sample solution was prepared in a mixture of acetonitrile and methanol (1:1).

The DTA measurements were taken using a METTLER, STAR^e SW 8.10 derivatograph. The TG-DTA analysis was performed in an N$_2$ atmosphere with a heating rate of 10 K/min in the range of 300–600 K. The investigated powder sample mass was 390 000 mg.

The electron paramagnetic resonance (EPR) spectra were recorded on a conventional X-band Bruker ELEXSYS E 500 CW-spectrometer operating at 9.5 GHz with a 100 kHz magnetic field modulation. The investigated samples were in a fine powder form. The first powder absorption spectra derivative was recorded as a function of the applied magnetic field. The EPR spectra temperature dependence in the 3–300 K temperature range was registered using an Oxford Instruments ESP helium-flow cryostat. The temperature dependence analysis of the following spin-Hamiltonian parameters was conducted: the EPR integrated intensity, calculated as a double integral of the EPR signal proportional to the imaginary part of the spin system's complex magnetic susceptibility; the g-factor, reciprocal of the integrated intensity, and the product of $T * I_{int}$ which was proportional to the square of the spin system magnetic moment. All the registered EPR spectra of the investigated complexes were simulated using the EPR–NMR computer program in order to study the above mentioned spin-Hamiltonian parameters. The anisotropic g-factors were calculated using the SIMPOW software package [11] in the temperature range of 3–55 K to extract the symmetry of the crystal field acting on the cation ion in the complex.

3. Results and discussion

3.1. Structure of MSB and MaSB ligands

Generally speaking, the complexes between a Schiff (MSB or MaSB) base macrocycle or its derivatives and lanthanide ions obtained by a template synthesis are characterized by high coordination numbers 7, 8 or 9 in which the coordination sites are substituted by such counterions as NO$_3$, ClO$_4$, SCN$^-$ or OAc$^-$ and H$_2$O or by solvent molecules [12–14]. If MSB (MaSB) complexes or their analogs with lanthanides include a water molecule, they can be coordinated to the cation or encapsulated in a cage formed by the ligand [14,15]. The coordination geometry in the complexes is different and depends on the coordination number, the complex type and the counterion kind (e.g. eight-coordinated Eu^{3+} complexes are distorted dodecahedrons [14] while the coordination geometry for nine-coordinated Nd^{3+} and Dy^{3+} complexes is a monocapped-square antiprismatic and monocapped-dodecahedron, respectively [16,17].

The $C_{39}H_{48}N_8O_3$ ligand structure is formed by: six aliphatic chains of CH$_2$, three OH phenolic groups, three CH$_3$ methyl groups, six imine C=N groups and two aliphatic nitrogen atoms. The $C_{27}H_{27}N_4O_3Cl_3$ ligand structure is formed by three aliphatic chains begining with an aliphatic nitrogen atom, three imine groups, three aromatic rings, three phenolic groups and three chlorine atoms. Aromatic rings are joined with aliphatic chains by imine groups. Phenolic groups and chlorine atoms are adjoined to aromatic rings.

3.2. Infrared spectroscopy

The ν(C=N) vibration mode in the Schiff base MSB-Gd^{3+} ligand was observed at 1638 cm^{-1} and confirmed the bicyclic condensation reaction with the consequent formation of a macrobicycle Schiff base. It was moved to higher wavenumbers (by about 12 cm^{-1}) after complexation. The ν(C=N) stretching mode shift towards higher wavenumbers indicates a stronger double bond nature of the iminic bonds and a coordination of the azomethine group nitrogen to the metal ion [18]. The phenolic ν(OH) vibration was moved towards lower frequencies from 3449 to 3420 cm^{-1} after complexation (compare Figs. 1 and 2 and Table 1). This indicates that the phenolic OH oxygen is coordinated to the metal ion. A band was observed for the complex at 3420 cm^{-1} which indicates that there is another water molecule in the complex. In addition to that, two wide bands assigned to M–N and M–O bonds were
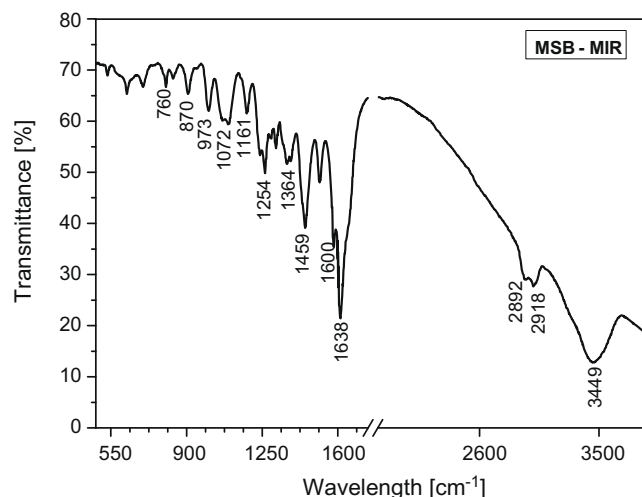

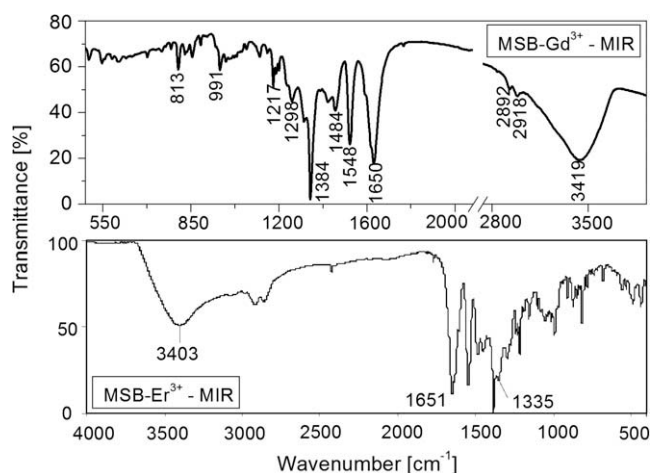**Fig. 1.** FT-IR trnsmittance spectrum of a macrobicyclic (MSB) ligand.

Fig. 2. FT-IR spectrum of MSB-Gd^{3+} and MSB-Er^{3+} complexes pressed into KBr pellets.
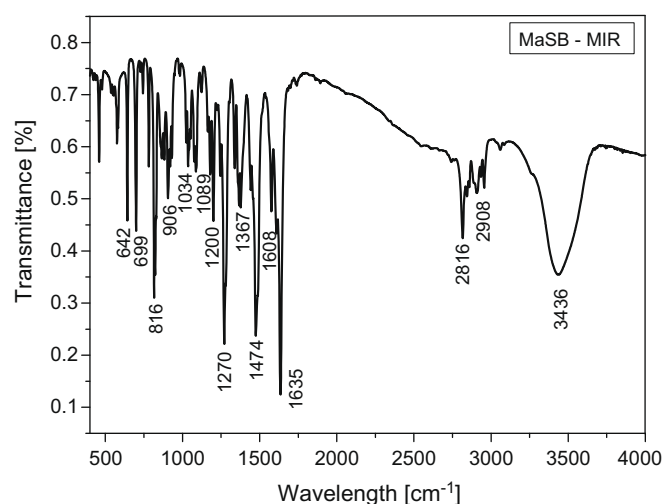

Fig. 3. Transmittance spectrum of an MaSB ligand.

observed in the FIR spectrum of the Gd complex at 395–489 cm^{-1} and 532–590 cm^{-1} [18–24], respectively.

The MSB-Er^{3+} complex spectrum in the KBr pellet shows a broad band at 3403 cm^{-1} which can be assigned to ν(OH) vibrations of a water molecule hydrogen bonded within the [(MSB-H + NO$_3$ + H$_2$O) Er]$^+$ complex [25]. The position of this band suggests that the water molecule within the complex is only weakly hydrogen bonded which can mean that the water molecule does not coordinate the metal cation. All the OH phenolic groups within the complex are involved in intramolecular hydrogen bonds with the respective nitrogen atoms of the Schiff base. Such conclusion finds confirmation in earlier CP-MAS studies [26] demonstrating formation of OH···N intramolecular hydrogen bonds in which the proton is localized at the oxygen atom as well as in a broad band in the FT-IR spectrum in the region of about 3000–2000 cm^{-1}. Furthermore, the appearance of two intense bands, assigned to the ν(C=N) vibrations at 1651 and 1638 cm^{-1} confirms the above statement. The band at 1651 cm^{-1} can be assigned to the stretching vibrations of Schiff base group complexes to the Er^{3+} cation and the other band at 1638 cm^{-1} can be assigned to the intramolecular hydrogen bonded groups as in a pure ligand. The presence of an NO$_3^-$ group as a ligand in the coordinating sphere is indicated by the appearance of a broadened band at ca. 1355 assigned to the ν(NO$_3$) vibrations overlapped with the bands assigned to the δ_s(CH$_3$) vibrations.

When comparing the IR spectra of different MSB complexes (Gd, Er) it can be found that they are very similar to each other.

A ν(C=N) stretching bond in the MaSB ligand and in the MaSB-Gd complex was observed at 1635.2 and 1625 cm^{-1}, respectively (see Fig. 3 and Table 2). This indicates that the azomethine group nitrogen is coordinated to the rare earth ion [27]. The phenolic ν(OH) stretching bond was observed at 3436 and 3432 cm^{-1} in the ligand and in the Gd complex, respectively in case of the complex powder mixed with KBr and pressed into pellets. This band was not observed for powder immersed in a poly(chlorotrifluoro-

ethylene) emulsion placed between CaF$_2$ plates. It indicates that the phenolic OH group observed in the IR spectrum of a MaSB-Gd complex comes from KBr.

A broad band in the region of 3000–2000 cm^{-1} occurs in the MaSB spectrum (see Fig. 3). This band is assigned to the stretching vibrations of protons getting involved in the medium-strong intramolecular N···H–O hydrogen bonds [28]. This band is not observed any longer in the MaSB-Dy^{3+} complex spectrum (see Fig. 4) indicating that all phenolic groups are deprotonated and that they are involved in the Dy^{3+} cation complexation process [29]. Furthermore, this spectrum indicates that no water molecules are present in the metal cation coordination sphere, either. It is only one band as a superposition of several bands assigned to ν(C=C) of aromatic rings and ν(C=N) of Schiff base vibrations that appears at 1635 cm^{-1} in the ligand spectrum in the region of 1650–1550 cm^{-1} [28,30]. A band of ν(C=C) vibrations is still observed in the complex spectrum at 1638 cm^{-1} and a band of ν(C=N) vibrations is shifted towards 1625 cm^{-1} indicating that the Schiff base groups are not protonated and that they coordinate the Dy^{3+} cation within the complex structure.

As can be seen in Fig. 4 and Table 2, the positions of IR bands corresponding to the main bonds differ each other only slightly for different complexes (Sm, Dy, Gd).

3.3. Mass spectroscopy

A molecular peak appearing in the MSB-Gd complex mass spectrum as an isotope pattern which is typical for a compound containing one gadolinium atom has confirmed the [1:1] ligand and metal proportion in the sample [18].

Other peak clusters at m/z = 903 and m/z = 921 are found on the extended scale of the MSB-Er complex ESI spectrum recorded at cv = 30 V in addition to the main peaks at m/z = 422 and m/z = 842, [25]. The spectrum has confirmed the [1:1] proportion of ligand and metal in the sample. The low intensity of the signal at

Table 1
Positions of wavelengths assigned to specific vibrations found in an MSB ligand and an MSB-Gd complex from an IR spectrum.

MSB ligand		MSB-Gd		MSB-Er	
Vibrations	Wavelength (cm^{-1})	Vibrations	Wavelength (cm^{-1})	Vibrations	Wavelength (cm^{-1})
Δ(CH$_2$)	1364	δ(CH$_2$)	1360	ν(NO$_3$), δ_s(CH$_3$)	1355
ν(C=N)	1638	ν(C=N)	1650	ν(C=N)	1651, 1638
ν(OH)	3449	ν(OH)	3419	ν(OH)	3403

Table 2
Positions of wavelengths assigned to specific vibrations found in the MaSB ligand, MaSB-Gd and MaSB-Dy complexes from an IR spectrum.

MaSB		MaSB-Gd		MaSB-Dy	
Vibrations	Wavelength (cm^{-1})	Vibrations	Wavelength (cm^{-1})	Vibrations	Wavelength (cm^{-1})
ν(C=N)	1635	ν(C=N)	1625	ν(C=N)	1635, 1630, 1625
ν(OH)	3436	ν(OH)	–	ν(C=C)	1610–1450

m/z = 921 indicates that the water molecule is easily lost upon complex fragmentation. This observation demonstrates that the water molecule is rather bonded to the ligand atoms not involved in the lanthanide ion coordination.

A molecular peak of m/e = 717 has been observed in the MaSB-Gd complex EI spectrum which corresponds to a compound in which three protons have been replaced by one gadolinium atom [27]. The isotope pattern of a molecular peak is typical for a compound with one gadolinium atom. The main peak in the ES spectrum with an isotope pattern similar to the above mentioned molecular peak has been observed at m/e = 718 and assigned to a single-protonated species containing one Gd atom.

One signal at m/z = 722 in the range of cv = 10–70 V is observed in the MaSB-Dy complex ESI spectrum corresponding to the mono-protonated 1:1 Dy(tren-5Clsal) [29]. A comparison of the isotopic distribution observed in the spectrum with the distribution calculated for the signal at m/z = 722 has confirmed the presence of monoprotonated Dy(tren-5Clsal). The protonation occurs probably on the tertiary N amine atom.

3.4. TG-DTA analysis

A TG-DTA analysis carried out up to 600 K has revealed that there is a significant loss of the MSB-Gd sample mass at 520 K [18]. The loss of mass analysis has determined the presence of two water molecules in the inner coordination sphere of a metal ion. Thus, the TG-DTA profile indicates a nine-coordination of a gadolinium ion.

It follows from the TG-DTA analysis of an MSB-Er complex that it is only a small part of the total sample mass, namely about 2%, that is lost at about 393 K [25]. As the total MSB-Er complex molecular weight based on the mass spectrometry results is 921 and the molecular weight of one water molecule is 18, the ratio of the molecular weight of water to the total molecular weight equals about 0.02. It is the same value as that obtained from the TG-DTA analysis. It indicates that it is only a single H_2O molecule that is bonded in the MSB-Er complex structure. It follows from the ESI measurements that the water molecule does not coordinate with a metal atom but with a ligand.

The TG-DTA analysis has revealed no significant loss of the MaSB-Gd sample mass up to 699 K [27]. Thus, the TG-DTA profile confirms that there is no water coordination of the metal ion in a MaSB-Gd complex. Hence, Gd ion has a 7-fold coordination.

3.5. Semiempirical calculations

Semiempirical calculations were performed based on the IR, ESI and TG-DTA data by applying AM1d quantum calculations and the Win Mopac 2007 program and the molecular mechanics method (MM3, Hyper-Chem 7.5). Geometric optimization was performed with an unlimited gradient of the convergence algorithm, the convergence was limited to 0.001 kcal/mol. It allowed us to propose
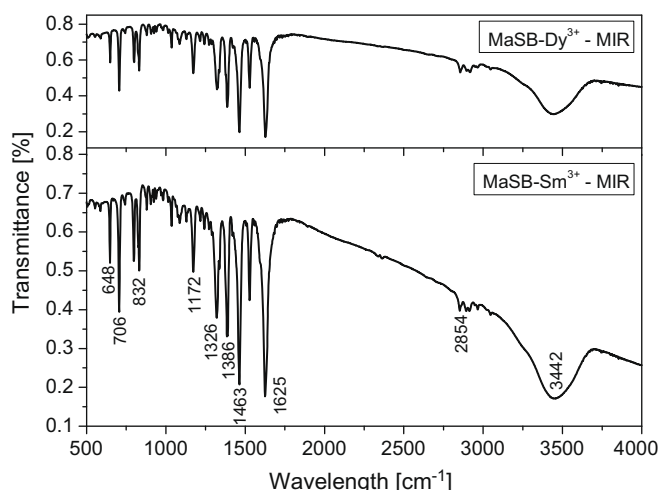

Fig. 4. FT-IR transmittance spectrum of MaSB-Dy and MaSB-Sm complexes.
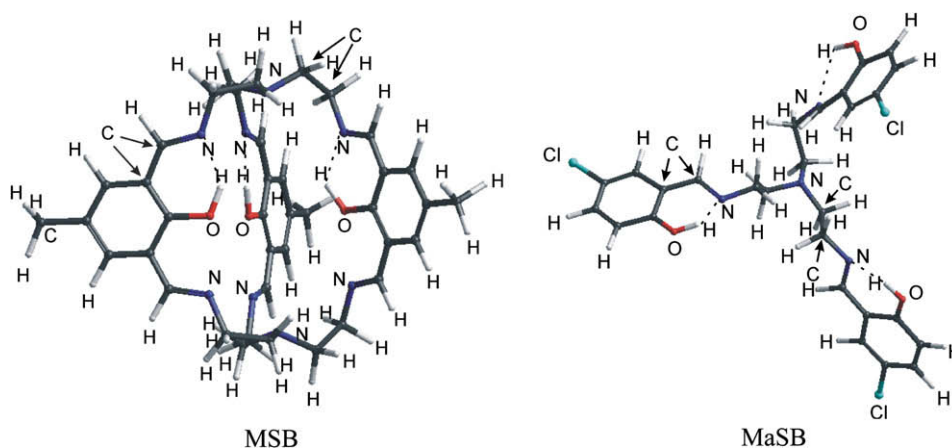

Fig. 5. Structure of MSB and MaSB ligands based on semiempirical calculations. Intramolecular bonds between nitrogen and hydrogen of phenolic group are marked by dotted lines.

structures of the investigated complexes. The structures are presented in Figs. 5 and 6.

The nearest neighborhood for an MSB Schiff base complex with e.g. erbium is formed by four nitrogen atoms: three from the imine group and one from the aliphatic group, and five oxygens: three oxygens from phenolic groups and two more from NO_3^- groups.

The nearest neighborhood for an MSB Schiff base with gadolinium is formed by four nitrogen atoms: three from the imine group and one from the aliphatic group, and by three atoms from the phenolic group. Two other oxygens come from water molecules.

The nearest neighborhood for a MaSB Schiff base complex with e.g. samarium is formed by four nitrogen atoms: three from the
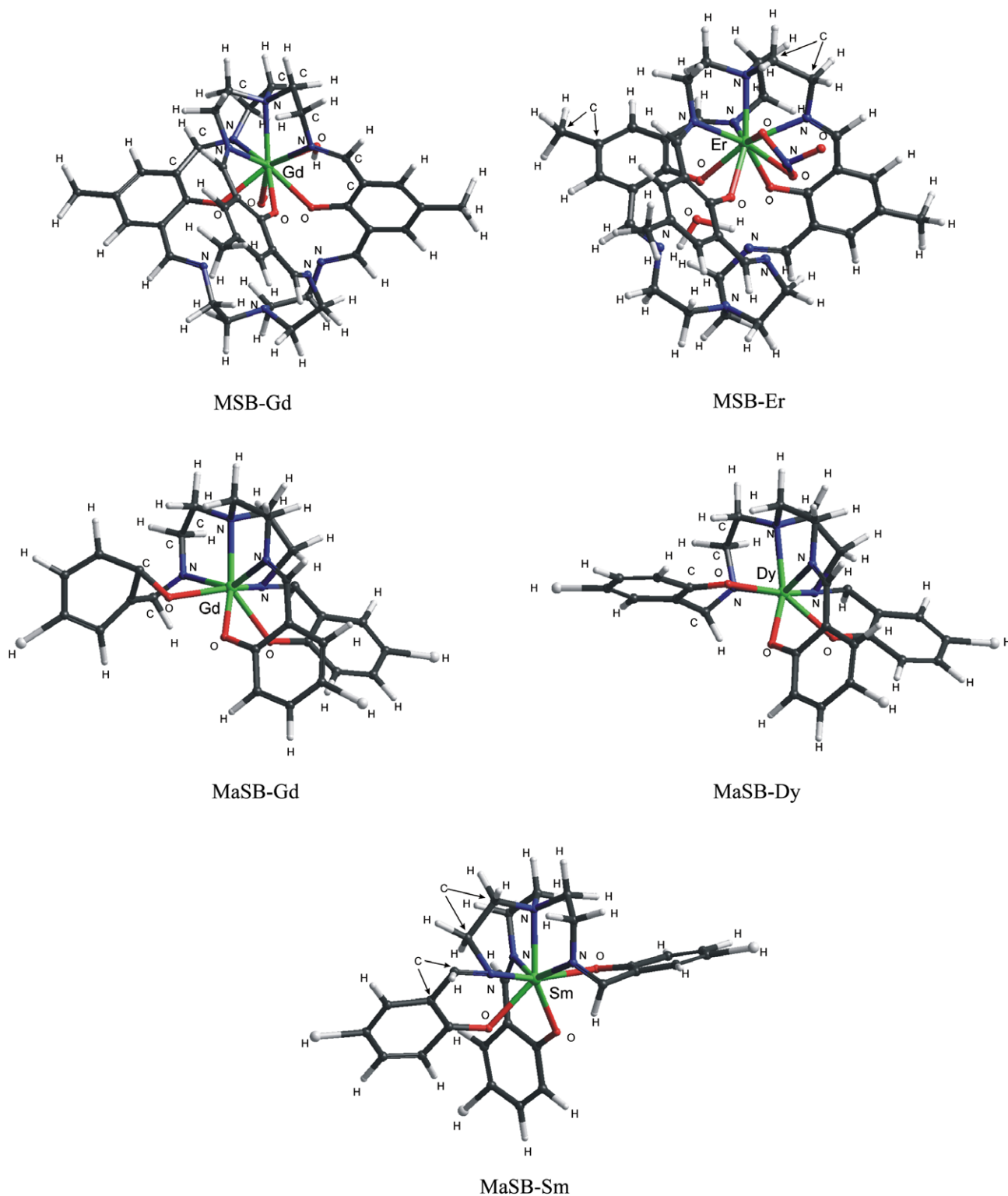
Fig. 6. Structures of MSB-Gd, MSB-Er and MaSB-Gd, MaSB-Dy, MaSB-Sm complexes based on the semiempirical calculations [31]. Only typical positions of carbon atoms are shown.

imine group and one from the aliphatic group, and by three oxygen atoms from the phenolic group. The same is valid for other investigated complexes (Gd, Dy).

The distances and angles between the nearest atoms of the cation ions in the investigated complexes were calculated and then plotted (see Tables 3 and 4 and Fig. 7). The coordination of Gd (Er) for MSB-Gd (Er) was found to be 9 (4 nitrogen atoms and 5 oxygens), while the coordination for MaSB-Gd(Dy, Sm) was 7 (4 nitrogen atoms and 3 oxygens).

3.6. Electron paramagnetic resonance

The following spin Hamiltonian can be used for a Gd(III) ion with a half-filled f shell with seven electrons and the ground state $^8S_{7/2}$:

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

where: 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 [20]. The number of parameters different from zero B_l^m depends on the site symmetry of the paramagnetic center.

The EPR signal for both MSB-Gd and MaSB-Gd complexes consisted of a main asymmetrical broad line with an unresolved structure centered at $g \sim 2$ and many additional unresolved lines at lower ($g \sim 6$) and higher ($g \sim 1.5$) magnetic fields [18,27]. The main peak amplitude at $g \sim 2$ for the MSB-Gd complex decreased on reducing the temperature from 300 to 160 K and increased upon further cooling to 3 K. The main peak amplitude for the MaSB-Gd complex centered at $g \sim 2$ decreased with the temperature decrease from RT to 3 K.

The presence of three different g_i components and non-zero values of many B_l^m parameters (for l = 2, 4, 6) was found by the fitting procedure. It indicates a low symmetry of the crystal field at the Gd site in the MSB-Gd complex. The presence of three different g_i components and non-zero values: B_l^m 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 in the second complex indicates a symmetry of a monoclinic type.

An analysis of the temperature dependence of the MSB-Gd complex EPR spectra (see Fig. 8, curve 1) shows that there is not any magnetically ordered state in this compound down to a temperature of 3 K. It is apparent that the thermal changes of I_{int} could not be described by a simple Curie–Weiss relation, $I_{int} = C/(T - \theta)$ over the whole investigated temperature range. There is a linear dependence of I_{int}^{-1} in the low temperature range of 3–25 K, and the Curie–Weiss relation in that range holds, with a practically zero value of the Curie–Weiss constant θ_{EPR} = −0.42(39) K. As a result, there are no magnetic interactions between MSB-Gd complexes below 25 K. However, the situation is quite different in a higher temperature range, T > 160 K. 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 complexes. This interaction might favor the formation of a certain number of short-lived ($T \sim 10^{-10}$ s on the EPR spectroscopy time scale) dimers with a non-magnetic S = 0 ground state and magnetic excited states. As the temperature decreases from RT, the population of excited states decreases and the population of non-magnetic ground state increases, decreasing in consequence the total magnetic moment of the system.

There is a linear dependence of I_{int}^{-1} (Fig. 8, curves 2, middle panel) in case of the MaSB-Gd complex below 130 K, and the Curie–Weiss relation in that range holds with the Curie–Weiss temperature θ_{EPR} = 10 K suggesting that there is a ferromagnetic interaction between MaSB-Gd complexes below 130 K. However, the situation is quite different in a higher temperature range, T > 190 K. 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 some of the Gd complexes as in the case of the MSB-Gd complex.

The following effective spin Hamiltonian for an effective spin of S = 1/2 has been applied for both MSB-Er and MaSB-Dy complexes:

$$H = \beta B \cdot g \cdot S, \qquad (2)$$

where all the symbols have their usual meaning.

The MSB-Er complex EPR spectra reveal two main spectral components [25]. The intensity of the spectral components decreased significantly with increasing temperature and they vanished completely above 60 K. Three rather very different values of g-factors along the paramagnetic complex principal axes such as e.g. g_x = 6, g_y = 12 and g_z = 4 calculated at 5.2 K were obtained using the SIMPOW program. It indicates a low symmetry site of the Er^{3+} ion in accordance with the above presented molecular mechanics and semiempirical calculations. The thermal dependence of g-factors evidences an increasing magnetic anisotropy of the complex with increasing temperature (see Fig. 9). An analysis of EPR spectra shows that the ground state is about 6.3 K below the excited state

Table 3
The nearest neighborhood of Gd and Er ions in MSB calculated using the WinMOPAC (PM5) and HyperChem (MM+) programs [31].

MSB-Gd^{3+}		MSB-Er^{3+}	
Bonds	Distance (Å)	Bonds	Distance (Å)
Gd–N0	2.365(2)	Er–O(1)	2.207(2)
Gd–N1	2.308(2)	Er–O(2)	2.218(2)
Gd–N2	2.300(2)	Er–O(3)	2.193(1)
Gd–N3	2.296(1)	Er–(O$_{NO_3^-}$)	2.265(2)
Gd–O1	2.241(2)	Er–O(O$_{NO_3^-}$)	2.242(1)
Gd–O2	2.250(1)	Er–N(3)	2.263(1)
Gd–O3	2.296(2)	Er–N(4)$_{mostek}$	2.329(2)
Gd–O4	2.251(2)	Er–N(6)	2.270(1)
Gd–O5	2.287(2)	Er–N(8)	2.268(2)
		Er–O$_{H_2O}$	–

Table 4
The nearest neighborhood of Gd, Dy and Sm ions in MSB calculated using the WinMOPAC (PM5) and HyperChem (MM+) programs [31].

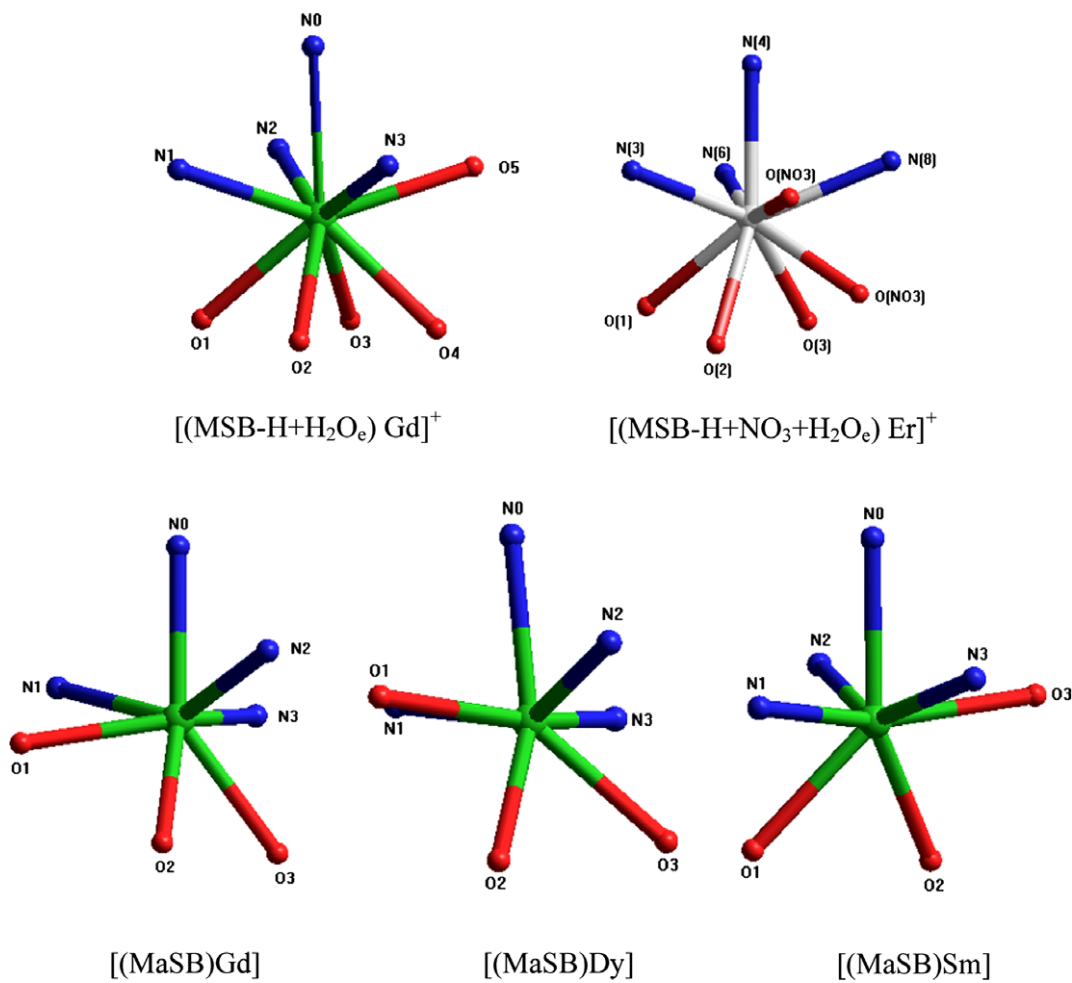| MaSB-Gd^{3+}		MaSB-Dy^{3+}		MaSB-Sm^{3+}	
Bonds	Distance (Å)	Bonds	Distance (Å)	Bonds	Distance (Å)
N0	2.324(2)	N0	2.3029(2)	N0	2.330(2)
N1	2.292(2)	N1	2.262(1)	N1	2.305(1)
N2	2.289(2)	N2	2.262(2)	N2	2.293(1)
N3	2.301(2)	N3	2.275(1)	N3	2.291(1)
O1	2.240(1)	O1	2.224(1)	O1	2.257(1)
O2	2.239(2)	O2	2.213(2)	O2	2.242(2)
O3	2.249(2)	O3	2.228(2)	O3	2.252(2)
Covalence radius, r = 161 pm		Covalence radius, r = 159 pm		Covalence radius, r = 162 pm	

Fig. 7. The nearest neighborhood of Gd, Dy and Sm cations in MSB and MaSb complexes [31].

that produces the EPR signal. An admixture of wave functions of the surrounding ions (especially large at high temperatures) into the Er^{3+} ion wave function may produce a non-magnetic ground state of the whole complex.

Two main spectral components in low magnetic field region (<300 mT) were observed in the MaSB-Dy complex EPR spectra for all the investigated temperatures [29]. The intensity of both spectral components increased significantly with a temperature decrease. The simulated spectra were reasonably close to the experimental ones, although a weak but persistent shoulder was not reproduced by simulation at about 280 mT. As a result of a
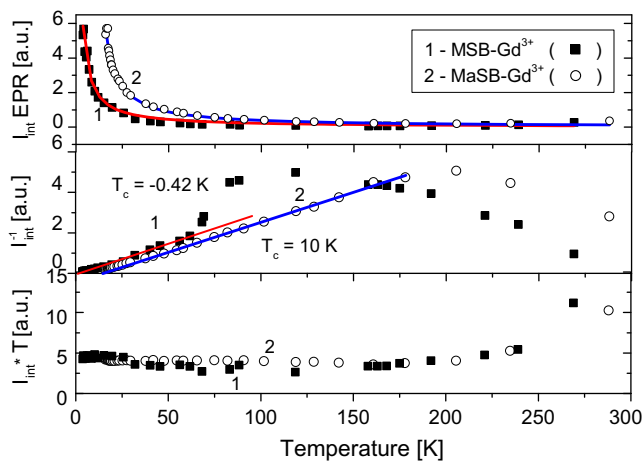

Fig. 8. EPR integrated intensity temperature dependence for MSB-Gd (1) and MaSB-Gd (2) complexes (upper panel) of the reciprocal integrated intensity (middle panel) and the product of $T \cdot I_{int}$ (lower panel). The solid lines in the upper panel mark Curie–Weiss relations, the straight lines in the middle panel mark the linear fitting of experimental results.
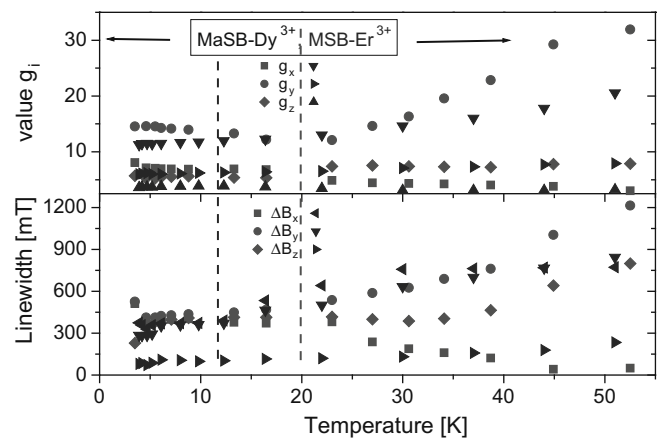

Fig. 9. Temperature dependence of the calculated anisotropic g_i-factors (upper panel) and anisotropic linewidths ΔB_i (lower panel) for MSB-Er and MaSb-Dy complexes.

simulation performed for low temperatures, an axial ($g_x = g_y \neq g_z$) symmetry of the paramagnetic center is less probable than an orthorhombic ($g_x \neq g_y \neq g_z$) symmetry (better fitting is observed at low magnetic fields).

The magnetic anisotropy between 3 and 23 K is practically constant as evidenced by an only marginal change of the g-factors spread, while the g_y factor increases strongly above 23 K with a temperature increase giving rise to a very high magnetic anisotropy of the complex at high temperatures (see Fig. 9). Our powder EPR spectrum of Dy^{3+} in MaSB-Dy seems to be 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 a thermal depopulation of the excited doublets below that temperature.

4. Conclusions

IR measurements and a TG-DTA analysis have evidenced the formation of MSB-Gd and MaSB-Gd complexes in which the Gd nearest neighborhood consists of nine ions: five oxygens and four nitrogens or seven ions: three oxygens and four nitrogens, respectively. A local symmetry at the Gd(III) site is low, almost monoclinic. The temperature dependence of I_{int} indicates that there is no magnetically ordered state in these compounds down to the temperature of 3 K. Strong antiferromagnetic interactions between Gd complexes are revealed in a high-temperature range, $T > 160$ K ($T > 190$ K) by the magnetic moment decreasing with a decrease in temperature. The interaction between Gd complexes might favor formation of short-lived dimers with a non-magnetic ground state for both complexes.

A variable-temperature EPR study of the MSB-Er^{3+} complex has revealed a low symmetry site of the Er^{3+} cation and a complicated pattern of magnetic interactions in this system. The thermal dependence of g-factors evidences an increasing magnetic anisotropy of the complex with increasing temperature. The observed low temperature drop of the integrated intensity (below 6 K) results from the existence of a non-magnetic ground state, 6.3 K below the excited states that produce the observed EPR signal.

The IR spectrum in MaSB-Dy powder samples indicates that the azomethine group nitrogen is coordinated to the rare earth ion. No bands characteristic for the $\nu(OH)$ vibrations have been found in the FIR spectrum which suggests that no water molecules are present in the coordination sphere of the metal cation. The thermal dependence of the g-factor evidences an increasing magnetic anisotropy of the complex with increasing temperature. The observed deviation from the integrated intensity Curie type behavior characterized by the Curie–Weiss constant $\theta_{EPR} = 30$ 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 at about 33(1) K above the ground state.

It should be emphasized that both MSB and MaSB complexes reveal an increasing magnetic anisotropy with increasing temperature especially with Er and Dy ions.

The MaSB complexes may catalyze reactions of toxic compounds and seem to be better candidates for synthetic enzymes. The advantage they have over natural enzymes is that they have fewer dimensions.

The results of investigations, showing a gadolinium coordination repletion in MSB-Gd complexes may be applied by manufacturers in pharmacology to produce a new contrast material for magnetic resonance imaging.

RE ions in macrocyclic complexes show a low symmetry. The magnetic properties of those complexes strongly depend on the kind of the paramagnetic ion which is isolated well enough from the neighboring ions by ligands. Thus, interactions between complexes are negligible.

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