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EPR STUDY OF GADOLINIUM(III) COMPLEXES WITH HETEROPOLYANIONS: $[Gd(SiW_{11}O_{39})_2]^{13-}$ AND $[GdP_5W_{30}O_{110}]^{12-}$

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The gadolinium complexes: $[Gd(SiW_{11}O_{39})_2]^{13-}$ [I] and $[GdP_5W_{30}O_{110}]^{12-}$ (Gd-encrypted Preyssler anion) [II] have been chosen for EPR study. This study is a continuation of our recent investigation related to solid gadolinium complexes: β-diketonates and aminopolycarboxylates. The EPR spectra of the Gd-polyoxometalates studied provide much better resolution than those recently studied. The spectra of Gd-polyoxometalates containing 1.7 to 2.5% of Gd(III) do not require an additional computer processing for correct interpretation. It is on the contrary to the β-diketonates and polyaminocarboxylates (with the content of Gd(III) 22–33%) for which the use of the RKU computer program (based on Fourier transform) was necessary in order to enhance the spectra resolution thus improving their correct interpretation. The EPR spectra obtained for the compounds I and II markedly differ from the U-spectrum characteristic of Gd(III) in glasses. Taking into account the spin-Hamiltonian calculations the existence of Gd(III) ion in two different surroundings: in a strong crystal field of rhombic symmetry and in a weak crystal field, is observed. The differences observed between the case I and II seem to be related to a various hydration degree.

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1. Introduction

Polyoxometalates are purely inorganic compounds which offer attractive properties as gadolinium(III) ligands. The significance and wide interest to the lanthanide(III)-heteropolyanions concern their potential antyviral activity and applications in catalysis [1]. Such complexes have potential applications in imaging and/or nuclear medicine. Rare earth elements are characterized by their $4f$-electrons. Therefore, it is interesting how $4f$-electrons contribute to chemical bonds and formation of complexes. Electron paramagnetic resonance is a very powerful method to study the magnetic properties and crystal field symmetry of rare earth complexes. Gadolinium with $4f^7$ electronic configuration ($^8S_{7/2}$), is the only trivalent lanthanide whose EPR can be observed in room temperature. The EPR study of the Gd^{3+} ion concerned only metal salts in which Gd has been introduced as dopant ($< 1\%$) into crystals. In our previous papers the EPR method was used for the first time to study the pure gadolinium complexes [2,3]. Because of the strong spin–spin interactions the EPR spectra obtained for such compounds were very broad and no details were possible to observe. Therefore, the special computer processing was used to enhance the spectra resolution and to observe the fine structure of the pure gadolinium compound spectra.

2. Experimental

2.1. Synthesis of compounds

The gadolinium-encrypted heteropolyanion $[GdP_5W_{30}O_{110}]^{12-}$ was prepared from the parent Preyssler anion according to the previously described method [1,4,5]. Substitution of Na^+ by Gd^{3+} was made according to the reaction

$$[NaP_5W_{30}O_{110}]^{14-} + Gd^{3+} \rightarrow [GdP_5W_{30}O_{110}]^{12-} + Na^+. \qquad (1)$$

The gadolinium sandwiched complex $[Gd(SiW_{11}O_{39})_2]^{13-}$ was obtained from the ligand $K_8[SiW_{11}O_{39}] \cdot 13H_2O$, which was prepared according to the method described by Jeannin and Martin-Frere [6]. Solid sample of $K_{13}[Gd(SiW_{11}O_{39})_2] \cdot 30H_2O$ was prepared by mixing concentrated solution of $GdCl_3$ (0.1 mol/l) with two equimolar amounts of warm solution containing $K_8[(SiW_{11}O_{39})_2] \cdot 13H_2O$. Potassium salt was obtained by addition of saturated KCl solution (to a concentration of $\approx$ 1 mol/l,) cooling the mixture to $\approx$ 278 K. The crystals were filtered off, washed with cold redistilled water and air-dried [7].

2.2. Methods

EPR spectra were recorded at room temperature as the first derivative of absorption using RADIOPAN spectrometer operating at 9.4 Ghz (X-band) microwave frequency with 100 kHz field modulation. The magnetic field was controlled with RADIOPAN JTM 41 digital NMR magnetometer.

3. Results and discussion

The Gd^{3+} ion doped into glasses exhibits an X-band EPR first-derivative spectrum characterized by three groups of lines with effective g-values of $\approx 6.0, 2.8$ and 2.0, and wide absorption band for magnetic fields corresponding to $g < 2$. This type of spectrum has been labelled as a U-spectrum in view of its *ubiquity* in vitreous materials [8] and in polycrystalline materials such as zeolites [9] and ceramics [10]. The first interpretation of the $g \approx 6.0$ feature of the U spectrum was given by Chepeleva and Lazurkin [11] who attributed it to a strong cubic field. Detailed analysis of the U-spectrum was also performed by Nicklin et al. [12]. They attributed these three features to the following kinds of crystal fields: weak cubic or a rhombic site ($g = 2.0$), intermediate crystal field ($g = 2.8$) and strong cubic field ($g = 6.0$). The alternative interpretation of the U spectrum was presented by Čugunov and Kliava [13]. They attributed the $g = 6.0$ feature to intermediate crystal field strength sites of axial symmetry, whereas the broadened appearance of the U-spectrum to the isolated rare earth ions in a wide variety of sites. A critical analysis of the ESR spectrum exhibited by the rare earth S-state ions, Gd^{3+} and Eu^{2+}, in glassy and disordered polycrystalline materials was given by Brodbeck and Iton [14]. It was found that all previous interpretations of the glassy spectra were unsatisfactory. The correct general solution of the spectrum is unequivocally established and shown to be a convolution of a broad and essentially unimodal distribution of second-order crystal field parameters b_2^0 and a broad distribution of asymmetry parameters $\lambda' = b_2^2/b_2^0$. The quantitative results indicate that the site symmetries of the rare earth ions are essentially very low and disordered, and are better characterized by a single low-symmetry "glassy type" site.

We used, for the first time, pure gadolinium complexes in EPR studies. Using the RKU computer program we could enhance the spectra resolution [15], make it possible to observe the fine structure of the powder spectra of gadolinium β-diketonates [2] and polycarboxylates [3]. The examples of the EPR spectra obtained for the $Gd(TTA)_3{\cdot}2H_2O$ complex, before and after the computer processing, are presented in Fig. 1 (A and B).

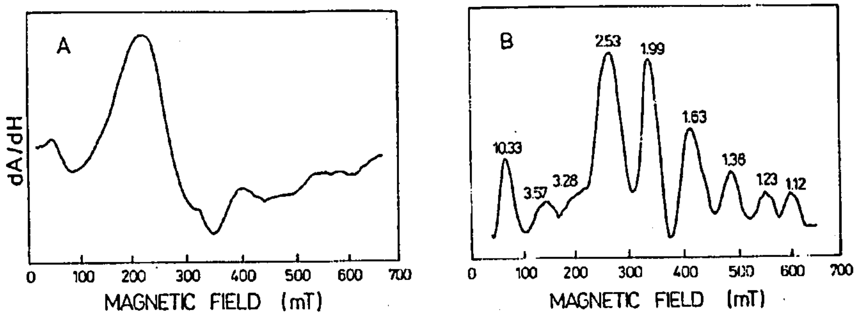

Fig. 1. EPR spectra of $Gd(TTA)_3 \cdot 2H_2O$. (A) The first derivative of absorption, (B) after the computer program processing.

In this paper a new group of gadolinium complexes with heteropolyanions as ligands has been chosen for the EPR study. Two polyoxometalates: the Preyssler anion and the heteropolyanion $[SiW_{11}O_{39}]^{8-}$ were selected. The Preyssler anion $[NaP_5W_{30}O_{110}]^{12-}$ can encapsulate the lanthanide(III) ions, via substitution of Na^+ by Ln^{3+}. The second ligand used is a lacunary compound $[SiW_{11}O_{39}]^{8-}$ formed from the plenary ligand $[SiW_{12}O_{40}]^{4-}$ by loss of one $[WO]^{4+}$ octahedral vertex. Such defected ligand forms with gadolinium a complex in which the Gd^{3+} ion is sandwiched between the defect site of two ligands as the composition of $[Gd(SiW_{11}O_{39})_2]^{13-}$. Using the Eu(III) luminescence lifetime measurements (in H_2O and D_2O) the following facts were found: no inner sphere H_2O's in the 1:2 complex of $[Eu(SiW_{11}O_{39})_2]^{13-}$ in aqueous solution and in the solid state [5, 16], and 3 inner sphere H_2O's in the case of europium-encrypted Preyssler anion, both in aqueous solution and the solid [4, 5]. In the case of the gadolinium-encrypted complex the Gd^{3+} ion is unsymmetrically encapsulated with two bounded (probably linearly) water molecules and most likely the third water molecule is not directly encrypted [4,5]. The symmetry of the gadolinium sandwich complex is probably lower than that of gadolinium-encapsulated one.

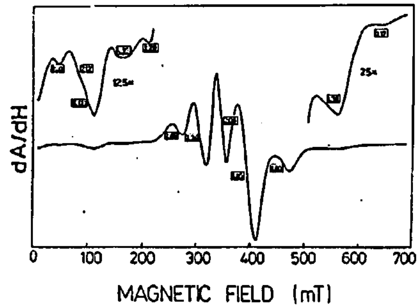

Fig. 2. EPR spectrum of $[GdP_5W_{30}O_{110}]^{12-}$ recorded as first derivative of absorption.

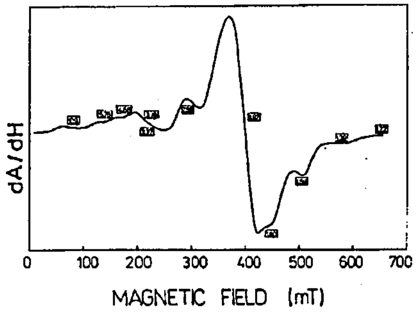

Fig. 3. EPR spectrum of $[Gd(SiW_{11}O_{39})_2]^{13-}$ recorded as first derivative of absorption.

The EPR spectra of gadolinium complexes: $[Gd(SiW_{11}O_{39})_2]^{12-}$ and $[GdP_5W_{30}O_{110}]^{12-}$ are presented in Figs. 2 and 3. The EPR spectra of the compounds studied have much better resolution than those recently studied. This is related to a lower amount of gadolinium contents in the compositions used. In such cases the spin–spin interactions between ions are smaller and therefore the spectra are better resolved. The spectra of Gd-polyoxometalates studied, containing 1.7 to 2.5% of Gd(III), do not require an additional computer processing for correct interpretation. It is on the contrary to the β-diketonates and polycarboxylates (with the content of Gd(III) 22–33%) for which the use of the RKU computer program (based on Fourier transform) was necessary in order to enhance the spectra resolution thus improving their correct interpretation. The EPR spectra obtained for the gadolinium polyoxometalates also markedly differ from the U-spectrum characteristic of Gd(III) in glasses [11]. The EPR spectrum recorded for the gadolinium sandwich complex (Fig. 2) consists of 11 lines with g-values: 10.9, 5.75, 4.68, 3.76, 3.37, 2.59, 1.97, 1.80, 1.59, 1.39 and 1.22. For the gadolinium-encrypted complex the EPR spectrum shows 12 lines (Fig. 3) with the following g-values: 11.0, 7.12, 6.00, 4.35, 3.28, 2.65, 2.34, 2.08, 1.85, 1.60, 1.38 and 1.17. The g-values of all until now performed EPR measurements of pure powder of gadolinium complexes are collected in Table.

TABLE

The g-factor values of particular EPR lines obtained for pure gadolinum β-diketonates, polikarboxylates and polyoxometalates.

$Gd(BAC)_3$ $\cdot 2H_2O$	$Gd(TTA)_3$ $\cdot 2H_2O$	$Gd(acaa)_3$ $\cdot 3H_2O$	Gd-POM encrypted	$Gd(POM)_2$ sandwiched	Gd(EDTA) $\cdot 3H_2O$	$Gd(DGA)_3$
17.90	10.33	8.59	11.0	10.9		
			7.12			7.97
5.33		5.20	6.00	5.75		
			4.35	4.68		
3.57	3.57	3.92		3.76	3.80	
	3.28		3.28	3.37		
		2.99			2.97	
2.60 s	2.53 s		2.65	2.59	2.63	2.75
		2.38	2.34		2.25	
		2.07	2.08		2.03	
1.99 s	1.99 s			1.97 s		1.96 s
		1.89 s	1.85 s	1.80 w	1.82 s	1.76 w
1.60	1.63	1.64	1.60	1.59	1.57	1.56
1.38	1.38	1.46	1.38	1.39	1.43	
1.26	1.23	1.25	1.17	1.22		
1.01	1.12	1.06				1.04

s — strong line, w — weak line.

Comparison of the EPR spectra recorded for gadolinium-polyoxometalates with those recently published by us for β-diketonates [2] and polycarboxylates [3] leads us to the following conclusions:

1. Spectra of Gd-polyoxometalates are very similar to the EPR spectra of Gd-β-diketonates. Especially for $Gd(BAC)_3 \cdot 2H_2O$ the g-values are very close to those obtained for the $[Gd(SiW_{11}O_{39})_2]^{13-}$ complex, whereas g-values for the $[GdP_5W_{30}O_{110}]^{12-}$ complex are similar to those observed in the case of $Gd(acac)_3 \cdot 3H_2O$. The g-values < 2.0 are almost similar, and only the small differences are observed for $g > 2.0$. On the basis of this similarity and taking into account the spin-Hamiltonian calculations by Nicklin et al. [12] (like in our previous papers [2,3]), it is possible to suppose the existence of the Gd^{3+} ion in two different surroundings: in a strong crystal field of rhombic symmetry and in a weak crystal field.

2. It is characteristic that the complexes having two water molecules in the Gd^{3+} inner sphere in such compounds as β-diketonates (BAC and TTA), as well as in the $Gd(DGA)_3$ complex with no water in the inner sphere, show in the EPR spectra a line with the g value ≈ 1.99 typical of free Gd^{3+} ion. On the other hand, for all of the gadolinium complexes with three water molecules in the inner

gadolinium ion sphere (i.e. with acac, EDTA and the Preyssler anion), a strong line with the value of $g = 1.85$ is observed and a weak line with $g \approx 2.07$, whereas the line of $g = 1.99$ is not present. We assume that the third water molecule, due to an anisotropy effect causes such influence on the EPR spectra. This also means that the value of zero-field splitting parameter ZFS-/D/ increases.

3. In the case of the $Gd(acac)_3 \cdot 3H_2O$ complex a rhombic distortion (related to the presence of the third water molecule) [2] was observed, which was associated with a shift of the line of $g = 2.60$ value (for the $Gd(BAC)_3 \cdot 2H_2O$ complex) to the value of $g = 2.99$ (for the $Gd(acac)_3 \cdot 3H_2O$ complex). Since the EPR spectrum of the complex $[GdP_5W_{30}O_{110}]^{12-}$ is quite similar to that of $Gd(acac)_3 \cdot 3H_2O$ the presence of the lines characteristic of complexes of gadolinium having three water molecules in the inner coordination sphere of metal, i.e. $g \approx 1.85$, and $g = 3.00$ should be expected. In fact, it is not observed in the $[GdP_5W_{30}O_{110}]^{12-}$ complex, and instead the line of $g = 2.65$ appears, corresponding to the line of $g = 2.60$, which is typically observed for the complexes with two water molecules in the inner coordination sphere. This supports the most recent suggestion that the third water molecule in the $[GdP_5W_{30}O_{110}]^{12-}$ complex is not directly encrypted [2,3], and suggests the symmetry lowering.

4. The values of the zero-field splitting parameter D for the both complexes studied have been estimated. In the case of the $[Gd(SiW_{11}O_{39})_2]^{13-}$ complex the value of D is equal to ≈ 1050 MHz, whereas in the case of the $[GdP_5W_{30}O_{110}]^{12-}$ complex it is above 1150 MHz. It means that the effect of the crystal field is more evident in the case of $[GdP_5W_{30}O_{110}]^{12-}$. Complexation of gadolinium by the lacunary ligand (which had been formed from the plenary ligand by loss of one octahedral vertex $[WO]^{4+}$ before complexing with Gd^{3+}) does not affect the complex structure and its symmetry so strongly as does the gadolinium encapsulation process.

5. It was proved that after the computer processing with the use of the RKU program the EPR spectra resolution increases and reveals their fine structure. This procedure enables us to study the EPR spectra of gadolinium compounds of high gadolinium contents and therefore difficult in correct interpretation. The well resolved EPR spectra obtained for the gadolinium–polyoxometalate complexes are in good agreement with the earlier reported data.

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