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Electron Paramagnetic Resonance study of chosen gadolinium(III) sandwiched- and encapsulated-polyoxometalate complexes

Andrzej Szyczewski[a,*], Stefan Lis[b], Zdzislaw Kruczynski[a], Slawomir But[b], Marian Elbanowski[b], Jerzy Pietrzak[a]

[a]*Institute of Physics, Adam Mickiewicz University, Umultowska 85, 61-614 Poznan, Poland*
[b]*Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland*

Abstract

The gadolinium(III) complexes with polyoxometalates were studied using X-band Electron Paramagnetic Resonance (EPR) spectroscopy. We selected the following sandwiched complexes: $Gd(SiW_{11}O_{39})_2^{13-}$ [**I**], $GdW_{10}O_{36}^{9-}$ [**II**], $Gd(P_2W_{17}O_{61})_2^{17-}$ [**III**], and encrypted $[GdSb_9W_{17}O_{86}]^{16-}$ [**IV**], $[GdP_5W_{30}O_{110}]^{12-}$ [**V**]. The EPR spectra obtained for the compounds **I**–**III** and **IV**–**V** differ markedly from the U-spectrum characteristic for Gd(III) in glasses. The values of the zero-field splitting parameter D for both kind of complexes studied have been estimated. 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**–**III** and **IV**–**V** seems to be related to a various coordination of the Gd(III) ion and its hydration degree. Our study shows a relation between the presence of particular g-values of the spectral lines and the number of the inner-sphere water molecules as well as the type of the Gd(III) complex (sandwiched and/or encrypted) in solid.

Keywords: EPR; Gadolinium; Polyoxometalate complexes; Crystal field

1. Introduction

Polyoxometalates (POMs), are purely inorganic compounds which offer attractive properties as gadolinium(III) ligands. The investigation of lanthanide complexes with POMs has important significance for their wide applications in catalysis, photochemistry, electron microscopy and medicine (antiviral activity and potential imaging-contrast agents) [1]. It is also a very interesting problem to elucidate the role and nature of the 4f-elements in coordination chemistry. Electron Paramagnetic Resonance (EPR), 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 at room temperature. The EPR study of the Gd^{3+} ion concerned only metal salts in which Gd had been introduced as dopant ($<1\%$) into crystals. In our previous papers, the EPR method was used to study the pure gadolinium complexes [1–3]. 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, a special computer processing was used to enhance the spectra resolution and to observe the fine structure of the pure gadolinium compound spectra. In this work, the EPR spectra of five Gd(III)–POM complexes, as polycrystalline powder, were measured and the effects of the coordinating ligands investigated. The crystal field and the symmetry are summed up and some relative regularities discussed.

2. Experimental details

2.1. Synthesis of compounds

The gadolinium(III) sandwiched complexes $Gd(SiW_{11}O_{39})_2^{13-}$ [**I**] and $Gd(P_2W_{17}O_{61})_2^{16-}$ [**III**], were obtained from the appropriate ligands, e.g., $K_8[SiW_{11}O_{39}]\cdot 13H_2O$ and $K_{10}[P_2W_{17}O_{61}]\cdot 20H_2O$, which were prepared according to the methods described by Jeannin and Martin-Frere [4]. The compound of $GdW_{10}O_{36}^{9-}$ ($=Gd(W_5O_{18})_2^{9-}$) [**II**] was synthesized, as described by Peacock and Weakley [5], from a solution containing gadolinium perchlorate and Na_2WO_4 of molar ratio 1:10. Solid samples of [**I**] and [**III**] compounds were prepared by mixing a concentrated

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*Corresponding author.

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solution of $GdCl_3$ (0.1 mol/l) with two equimolar amounts of warm solution containing $K_8[SiW_{11}O_{39}]\cdot 13H_2O$ or $K_{10}[P_2W_{17}O_{61}]\cdot 20H_2O$. Potassium salt was obtained by addition of saturated KCl solution (to a concentration of ~1 mol/l) and cooling the mixture to ~278 K. The crystals were filtered off, washed with cold redistilled water and air-dried [6].

The gadolinium-encrypted heteropolyanion $[GdSb_9W_{17}O_{86}]^{16-}$ [**IV**], $GdP_5W_{30}O_{110}]^{12-}$ [**V**] complexes were prepared from the compounds of $(NH)_{16}[NaSb_9W_{21}O_{86}]\cdot 24H_2O$ and the parent Preyssler anion $K_{12.5}Na_{1.5}[NaP_5W_{30}O_{110}]\cdot 20H_2O$, which were synthetized according to the previously described method [4] and [4,7,8], respectively. Substitution of Na^+ by Gd^{3+} in these structures was made as according to procedures [9] for $[GdSb_9W_{17}O_{86}]^{16-}$ and [10–12] for $GdP_5W_{30}O_{110}]^{12-}$.

2.2. Methods

EPR spectra were recorded at room temperature as the first derivative of absorption using a 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

Three gadolinium sandwiched $Gd(SiW_{11}O_{39})_2^{13-}$ [**I**], $GdW_{10}O_{36}^{9-}$ $(=Gd(W_5O_{18})_2^{9-})$ [**II**], $Gd(P_2W_{17}O_{61})_2^{17-}$ [**III**], and two encrypted $[GdSb_9W_{17}O_{86}]^{16-}$ [**IV**], $[GdP_5W_{30}O_{110}]^{12-}$ [**V**] with POMs as ligands have been chosen for the EPR study. The polycrystalline powder EPR spectra (X-band) of Gd(III)–POM complexes were recorded at room temperature and examples of spectra are shown in Figs. 1–3. Their spectral parameters are presented in Table 1, together with the data obtained earlier for Gd-polycorboxylate and Gd-β-diketonate complexes.

The sandwiched complexes (**I**, **II** and **III**) are formed from the lacunary compounds, $SiW_{11}O_{39}^{8-}$ and $P_2W_{17}O_{61}^{10-}$, obtained from the plenary ligands $SiW_{12}O_{40}^{4-}$ and $P_2W_{18}O_{62}^{6-}$ by a loss of one $[WO]^{4+}$ octahedral vertex. Such a defected ligand forms with gadolinium a complex in which the Gd^{3+} ion is sandwiched between the defect site of two ligands. Using the Eu(III) luminescence lifetime measurements (in H_2O and D_2O) the following were found: no inner sphere H_2O molecules in the sandwiched complexes, both in aqueous solution and in the solid state. In the case of gadolinium-encrypted complexes (**IV** and **V**), the Preyssler $[NaP_5W_{30}O_{110}]^{12-}$ and the 'HPA-23' $[GdSb_9W_{17}O_{86}]^{16-}$ anions can encapsulate the lanthanide(III) ions, via substitution of Na(I) by Gd(III). These compounds, both in aqueous solution and the solid [12,13] are encapsulated with three- and four-bounded water molecules, as Eu(III) luminescence lifetime measurements shown. In the case of the Gd-encrypted Preyssler complex the Gd(III) ion is unsymmetrical with two bonded water molecules and most likely the third water molecule is not directly encrypted [11,12].

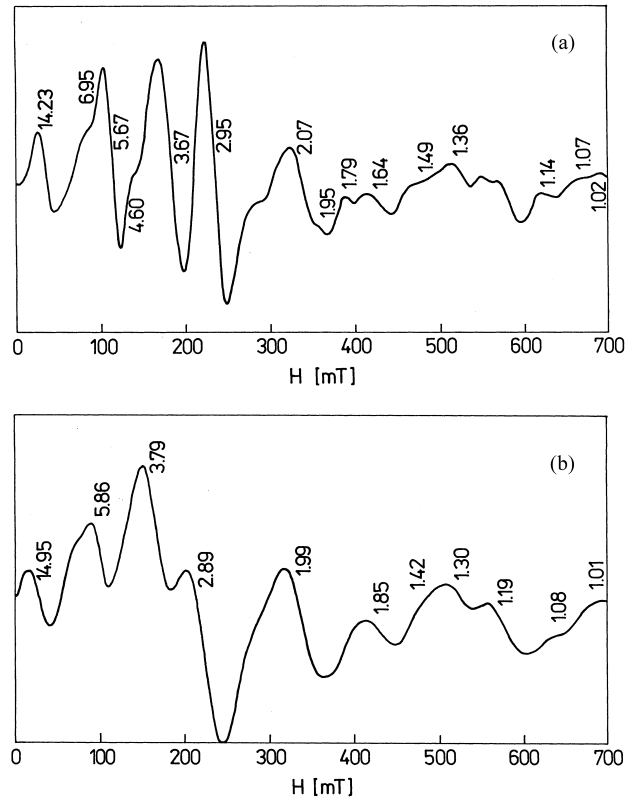

Fig. 1. EPR spectra of $[GdW_{10}O_{36}]^{9-}$ [**II**] recorded, 2 days (A) and 30 days (B) after synthesis, as first derivative of absorption.

The spin Hamiltonian for Gd(III) ion can be written as:

$$H = H_{\mathrm{ZEEMAN}} + H_{\mathrm{CF}} = g_0 \beta B \cdot S + D[S_z^2 - (1/3)S(S+1)] + E(S_x^2 - S_y^2), \tag{1}$$

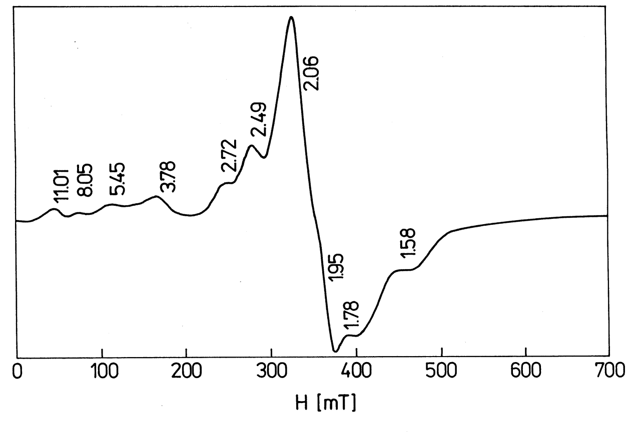

Fig. 2. EPR spectrum of $[Gd(P_2W_{17}O_{61})_2]^{16-}$ [**III**] recorded as first derivative of absorption.

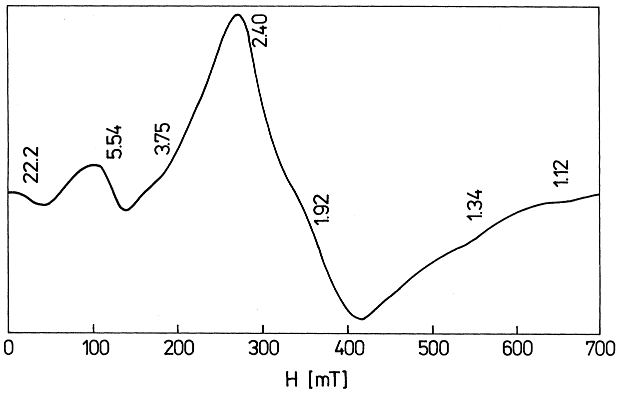

Fig. 3. EPR spectrum of $[GdSb_9W_{17}O_{86}]^{16-}$ [**IV**] recorded as first derivative of absorption.

where the g-value of the (S-state) ion is isotropic and equal to g_0 as in the free ion. D and E are the zero field-splitting constants and H_{CF} is the effective crystal-field interaction term. The value of parameter D was found from Eq. 1 using the second order perturbation calculus. Exact calculation of D and E requires a full simulation of EPR spectrum for the powdered sample performed on the basis of exact solutions of Eq. 1. Such a simulation will be made by a special computer program which is under preparation at present, and its results will be published in our subsequent paper.

The EPR spectra of the Gd–POM complexes studied have much better resolution than those recently studied [1,2]. 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 ~1.6 to ~5.2% of Gd(III), do not require an additional computer processing for correct interpretation. The EPR spectra obtained for the gadolinium polyoxometalates also differ markedly from the U-spectrum characteristic for Gd(III) in glasses [14]. The EPR spectrum recorded for the gadolinium sandwich (**I**) complex consists of 11 lines (with g-values: 10.7, 5.74, 4.68, 3,78, 3.37, 2.59, 1.97, 1.79, 1.59, 1.39 and 1.22) and complex (**III**) (Fig. 2) 10 lines (with the following g-values: 11.01, 8.05, 5.45, 3.78, 2.72, 2.49, 2.06, 1.95, 1.79 and 1.58) as shown in Table 1. In the case of the compound (**II**) the EPR spectrum (Fig. 1) differs from all other spectra recorded and shows sixteen very well separated lines. Spectra obtained for encrypted–gadolinium compounds (**IV**) and (**V**), presented as an example in Fig. 3 for (**IV**), have 7 and 13 lines with g-values, respectively, as shown in Table 1.

Analysis of the EPR spectra recorded for Gd(III)–POM complexes leads us to the following conclusions:

- The spectrum of the sandwiched compound (**II**) differs markedly from all other recorded for the compounds studied, especially the intensity of the lines in the range of a low magnetic field is much higher as compared to the middle and higher values of magnetic field. So that, a high value of zero-field splitting (ZFS) parameter, D, should be expected. The value of D, estimated as 2400 MHz, is indeed much higher than those obtained for all other complexes. In our previous EPR studies related to Gd(III) compounds (β-diketonates and aminopolycarboxylates) such spectra were not observed as well. In the case of sandwiched structures (**I**) and (**III**), the lowest effect of the crystal field appeared and the ZFS parameter D was determined as 1050 MHz. The encrypted structures (**V**) and (**IV**) with D estimated as 1150 and 1250 MHz, respectively, show stronger effect of the crystal field than compounds (**I**) and (**III**).

Table 1
The g-factor values of particular EPR lines obtained for pure gadolinum polyoxometalates, polycarboxylate and diketonate

$Gd(SiW_{11}O_{39})_2^{13-}$ **I**	$GdW_{10}O_{36}^{9-}$ **II**	$Gd(P_2W_{17}O_{61})_2^{17-}$ **III**	$[GdSb_9W_{17}O_{86}]^{16-}$ **IV**	$[GdP_5W_{30}O_{110}]^{12-}$ **V**	$Gd(EDTA)\cdot 3H_2O$	$Gd(acac)_3\cdot 3H_2O$
10.7	14.23s	11.01	22.2	11.0		8.59
	6.95	8.05	7.12			
5.74	5.67s	5.45	5.54	6.00		5.20
4.68	4.60			4.35		
3.78	3.67s	3.78	3.75		3.80	3.92
3.37				3.28		
	2.95s	2.72			2.97	2.99s
2.59		2.49		2.65	2.63	
			2.40	2.33s	2.25	2.38
	2.07s	2.06s		2.08s	2.03	2.07
1.97s	1.95s	1.95				
1.79w	1.78	1.79	1.92	1.85s	1.82s	1.89s
1.59	1.64	1.58		1.60	1.57	1.64
1.39	1.36		1.34	1.38, 1.34	1.43	1.46
1.22	1.29, 1.23, 1.14		1.12	1.17		1.25
	1.07, 1.02					

s = strong line; w = weak line.

- The *D* values indicate that the presence of heteroatoms (P, Si and Sb) in the polyoxometalate structure may lead to an increase of the system symmetry.
- In the case of compound (**II**), EPR spectra recorded after a few weeks, showed a broadening of all lines (Fig. 1a b), but the mechanism of this phenomenon is still not clear.
- A comparison of the EPR spectra of the Gd(III)-encrypted complexes (**IV**) and (**V**), having 3 and 4 water molecules in the inner-coordination sphere, with previously studied (β-diketonates and aminopolycarboxylates) complexes [1,2] indicates similar *g* values as estimated in the case of compounds with 3 inner sphere H_2O molecules (e.g. $EDTA\cdot 3H_2O$ and $Gd(acac)_3\cdot 3H_2O$). Two lines are positioned in the range of *g* 2.3–2.4 and 1.8–1.9 for such compounds. Structures with two or no water molecules in the inner sphere complexation of Gd(III) are characterized by one strong line of *g* 1.95–1.99.

Studies on the Gd(II)–POM systems are underway and we are going to use a spectral simulation for the $^8S_{7/2}$ system of Gd(III) ion, in order to determine more exact values of ZFS parameters *D* and *E*.

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