

Spectroscopic studies of Ln(III) complexes with polyoxometalates in solids, and aqueous and non-aqueous solutions

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ABSTRACT. Chosen polyoxometalate (POM) anions and their lanthanide(III) complexes, LnPOM, have been synthesized and spectroscopically characterized in solid state, aqueous and non-aqueous solutions. POMs, such as Keggin's, Dawson's and Anderson's type, $\text{Na}_9\text{EuW}_{10}\text{O}_{36}$, compositions that function as inorganic cryptands ($[(\text{Na})\text{P}_5\text{W}_{30}\text{O}_{110}]^{14-}$ -Preyssler anion, and $[(\text{Na})\text{As}_4\text{W}_{40}\text{O}_{140}]^{27-}$), containing inorganic (Na^+ , K^+ , NH_4^+) or organic (tetrabutylammonium, NBu_4^+) counter cations were obtained and their Ln(III) complexes (sandwiched and encapsulated) studied. The synthesized compounds were identified using elemental and thermogravimetric analysis, UV-Vis spectrophotometry and FTIR spectroscopy. The complexation studies were carried out with the use Nd(III) and Er(III) optical absorption and Eu(III) luminescence spectroscopy. Luminescence characterization, including results of intensity, quantum yields and luminescence lifetimes of EuPOM complexes in aqueous, non-aqueous solutions (DMF, DMSO, acetonitrile) and solid are discussed. Based on luminescence lifetime measurements of the Eu(III) ion the hydration numbers of its sandwiched (efficient emitters) and encrypted complexes have been determined and quenching effect discussed. The Eu(III) complexes entrapped in a xerogel matrix have been studied as luminescent materials. Luminescence intensity, lifetime and quantum yield of the EuPOM materials and their photochemical stability, during continuous UV irradiation, were tested.

1. INTRODUCTION

The majority POMs composed of molybdenum and tungsten polyhedrons, due to their interesting physicochemical properties, and biological importance, have been a subject of numerous studies. This class of compounds has received much attention in the last two decades because of their wide applications in catalysis, material engineering, photochemistry and in medicine. Their attractive and often unusual physicochemical properties are related to their structure, shape, charge density, redox potential, acidic character and solubility. POMs with alkali counter cations such as Na^+ , K^+ and NH_4^+ are well water-soluble compositions. They can be solved in solvents of different polarity, depending on the kind of the counter cation occurring in the POM molecule [1-4]. Generally POMs can be categorized into three structural groups, depending on the coordination number of the heteroatom [1, 2]. Our previous studies concerned synthesis of POMs and their Ln(III) complexes, representing the three structural groups of POMs and additionally so-called inorganic analogues of crown-ethers and cryptands (e.g. Preyssler's anion). They have been characterized using spectroscopic methods both in aqueous [2, 5-8] and non-aqueous solutions [9]. Some of LnPOM complexes show interesting and effective luminescence properties, i.e. high luminescence intensity, its quantum yields

and long lifetimes of Ln(III) excited states [10]. Such complete inorganic materials, particularly EuPOM complexes, have been entrapped in xerogel matrices by sol-gel method and examined as luminescent materials. The resulting immobilization of Eu(III) complexes in xerogel matrices is known to enhance emission intensity [11, 12]. These luminescent materials have been also tested for their photochemical stability under continuous UV irradiation.

2. EXPERIMENTAL

2.1. Methods. All reagents used in these studies were at least analytical grade, while Nd_2O_3 and Eu_2O_3 were spectroscopically pure and non-aqueous solvents (DMF, DMSO, acetonitrile, dichloromethane from Fluka) pure for UV spectroscopy (content of $\text{H}_2\text{O} < 0.005\%$). Elemental analysis of the POMs and their europium complexes were made with the use of an Elemental Analyser 2400 CHN, Perkin Elmer. Thermogravimetric (TG) and differential thermal (DTA) analysis were conducted using a Shimadzu TGA-50H/A50 thermoanalytic system, temperature interval was 293-823 K, heating rate 2 K/min in air atmosphere. Absorption spectra were recorded on a UV-2401PC Shimadzu spectrophotometer. The IR spectra were obtained by means of FTIR Bruker JFS 113v spectrophotometer for the samples ($\sim 2\text{mg}$) prepared in KBr. The corrected luminescence spectra of Eu(III) were recorded using

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Table 1. *The luminescence data of Eu(III) ion in EuPOM complexes in solutions, $\lambda_{\text{exc}} = 394 \text{ nm}$, $C_{\text{Eu(III)}} = 0.001 \text{ mol/l}$.*

Compound	Lifetime [ms]	Hydration number	Luminescence Intensity [a.u.],	Quantum yield
			$\lambda_{\text{max}} = 615 \text{ nm}$	
Eu(ClO ₄) ₃	0.11	9.3	0.01	2.60×10^{-3}
Na ₉ [EuW ₁₀ O ₃₆]	2.29	0.2	2.0 ^c	4.19×10^{-3}
K ₁₇ [Eu(P ₂ W ₁₇ O ₆₁) ₂]	3.08	0.1	0.4	1.38×10^{-2}
Eu ₂ TeMo ₆ O ₂₄	0.19	5.1	0.08	–
K ₂₅ [(Eu)As ₄ W ₄₀ O ₁₄₀]	0.25	3.7	0.02 ^d	9.06×10^{-3}
K ₁₂ [(Eu)P ₅ W ₃₀ O ₁₁₀]	0.30	3.1	0.23 ^e	9.6×10^{-5}
(NBu ₄) ₁₂ [(Eu)P ₅ W ₃₀ O ₁₁₀] ^a	0.79	0.6	0.37 ^e	1.1×10^{-4}
(NBu ₄) ₈ H ₃ [Eu(PMo ₂ W ₉ O ₃₉) ₂] ^b	1.11	0.2	0.95 ^f	–
K _{11,13} [Eu((P/Si)Mo _x W _{11-x} O ₃₉) ₂]	1.2–3.5 Ref. [6]	0.1	0.0–4.8 Ref. [6]	10^{-4} – 10^{-2} Ref. [18]

^a in acetonitrile, ^b in DMF, ^c $\lambda_{\text{max}} = 300 \text{ nm}$, ^d $C_{\text{Eu(III)}} = 1 \times 10^{-4} \text{ mol/l}$, ^e $C_{\text{Eu(III)}} = 1 \times 10^{-2} \text{ mol/l}$, ^f $\lambda_{\text{exc}} = 342 \text{ nm}$.

Table 2. *The luminescence characterization of EuPOM complexes entrapped to xerogels.*

HPAS	Type of matrix	Lifetime [μs],	Luminescence Intensity [a.u.],	Quantum yield
		$\lambda_{\text{exc}} = 394 \text{ nm}$	$\lambda_{\text{max}} = 615 \text{ nm}$	
Na ₉ EuW ₁₀ O ₃₆	SiO ₂	642.8	23.7*	0.123
	SiO ₂ – PDMS	491.9	19.8*	0.104
	SiO ₂ – TEG	508.4	24.4*	0.066
Eu ₂ TeMo ₆ O ₂₄	SiO ₂	245.9	15.3 ⁺	0.027
	SiO ₂ – PDMS	162.9	23.8 ⁺⁺	0.018
	SiO ₂ – TEG	275.4	37.6 ⁺⁺⁺	0.012

* $\lambda_{\text{exc}} = 394 \text{ nm}$, ⁺ $\lambda_{\text{exc}} = 320 \text{ nm}$, ⁺⁺ $\lambda_{\text{exc}} = 315 \text{ nm}$, ⁺⁺⁺ $\lambda_{\text{exc}} = 330 \text{ nm}$.

a Perkin-Elmer MPF-3 spectrofluorimeter. The luminescence lifetime of Eu(III) was measured with the use of the detection system described earlier, consisting of a nitrogen laser (KB6211) and a tunable dye laser [13]. The luminescence decay curves observed in this work were analyzed by a single exponential fitting, providing the decay constants. The luminescence quantum yield, Φ , of the Eu(III) ion in solution was calculated using [Ru(bpy)₃]Cl₂ as a standard. In the case of powder samples Φ was determined based on the procedure described by Wrighton *et al.* [14]. Measurement of luminescence quantum yields of the powder samples involved determination of the diffuse reflectance of the sample relative to a nonabsorbing standard (KBr) at the excitation length, and then measuring the emission of the sample under the same conditions [15]. The quantum yield is the ratio of the emitted photons to the difference in the number of diffuse reflected photons from the sample and the nonabsorbing standard, has been calculated using the equation (1):

$$\Phi = \frac{E}{R_{\text{std}} - R_{\text{smpl}}} \quad (1)$$

where E is the area of the corrected emission curve of the sample, R_{std} and R_{smpl} are corrected areas under the diffuse reflectance curves of the nonabsorbing standard and samples, respectively, at the excitation

wavelength. The calculated values of the luminescence quantum yields of the samples studied are given in Tables 1 and 2.

The Eu(III) complexes entrapped in xerogels were irradiated by means of a UV lamp of radiation power 0.53 W/cm^2 .

2.2. Synthesis and identification of compounds.

The lacunary structures of the heteropolyanions (for example SiW₁₁O₃₉⁸⁻) were obtained from the corresponding plenary structures (SiW₁₂O₄₀⁴⁻) as a result of their partial degradation as described earlier [16]. Europium sandwiched complexes Eu(POM)₂ were obtained according to the method described by Peacock and Weakley [17] and modified by us [18]. The cryptand analogues of the heteropolyanions and their Eu(III)-encrypted derivatives were prepared as previously described [5, 15, 19, 20]. Tetrabutylammonium salts of the chosen compounds was obtained with using a literature procedure [21]. Identification of synthesized compounds was done by comparison of the IR spectra of obtained compounds with those previously reported, elemental and thermogravimetric analysis [5–7, 18] and our own spectrophotometric method for determination of tungsten and molybdenum contents. The spectrophotometric method enables the simultaneous determination of W(VI) and Mo(VI) in

POMs and their Ln/POM complexes with disodium-1,2-dihydrobenzene-3,5-disulfate (Tiron), used as colorimetric reagent [22].

2.3. Synthesis of the POMs entrapped in sol-gel matrices. A wet gel product was obtained after some days by sol-gel process (hydrolysis and polycondensation) of tetramethoxysilane (TMOS) in mixture with methanol and aqueous solution of EuPOM complex [23]. Methylated silicate xerogels was synthesized in the similar way. A 1 : 1 mixture of TMOS (Aldrich) and polydimethylsiloxane (PDMS 200, Aldrich)) was dissolved in methanol and water as reagent was added [24]. In the case of TMOS and triethylenglycol (TEG) with 1 : 1 molar ratio, the components were dissolved in methanol, heated to 60 °C and stirred for ten minutes [25]. Then aqueous solution of EuPOM complex was added. In each gel preparation the molar ratio [alkoxidegroup] : [H₂O] = 1 : 1 and the resulting wet gels were dried at room temperature to obtain xerogels. The final concentration of the Eu(III) complexes in xerogels are 5×10^{-5} mol/g xerogel.

3. RESULTS AND DISCUSSION

The compositions of POMs were determined based on results of the elemental (C, N, H), thermogravimetric analysis (H₂O, [NH₄]⁺, [NBu₄]⁺, H⁺), spectrophotometric determinations of Mo and W in the range of UV-Vis, and FTIR spectra analysis. The elemental analysis was very useful in the case of POM compositions containing an organic counter cation.

The use of the FTIR spectroscopy has shown to be a very useful tool in studies of POMs and their complexes due to easy indication of the plenary, lacunary and of sandwich complexes, based on characteristic features of the spectra [6]. The formation of the lacunary structure (pH dependent degradation of an appropriate plenary structure) indicates a split of the P-Oa and W-Oc-W band oscillations, as a consequence of existence of two different coordination environments of phosphorus and oxygen atoms, Oc. FTIR spectroscopy has been used to fingerprint the POM structures because of good correlations between spectral peak positions, shapes, and relative intensities of the spectra, obtained for solid and solution. These correlations strongly indicate identical structures [18]. The FTIR spectra of tetrabutylammonium compositions of POMs have generally the same bands as the spectra recorded for the potassium or ammonium salts. Additional bands attributed to the C – H and C – C oscillations of the (NBu₄)⁺ organic species, in the range of 1300–1500 cm⁻¹ and 2800–3000 cm⁻¹, occur in this case.

Absorption spectra of Nd(III) and Er(III) in the range of their hypersensitive transitions $^4I_{9/2} \rightarrow ^2H_{9/2}$ and $^4I_{15/2} \rightarrow ^2H_{11/2}$, respectively, were measured for various metal:ligand ratios in non-aqueous solutions. Positions and intensities of the spectra are sensitive to

the ligand field of POMs and can be used to evaluate the formation of LnPOM complexes. Examples of the spectra, measured for various Ln(III) : POM molar ratios, ranging from 1 : 0 to 1 : 3, in DMSO and DMF solutions, are presented in Figures 1 and 2.

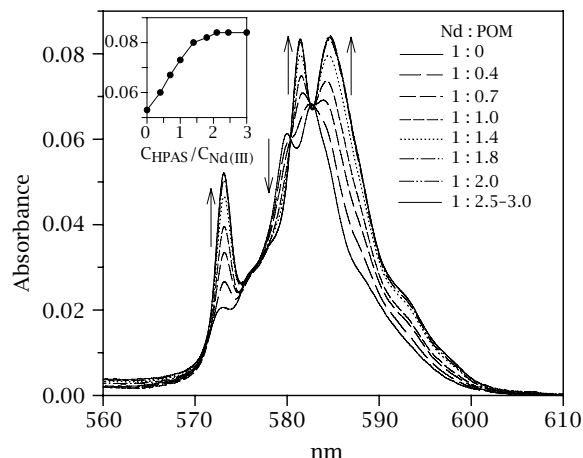


Figure 1. Absorption spectra of Nd(III) in the range of the hypersensitive transition ($^4I_{9/2} \rightarrow ^2H_{9/2}$) for various Nd : [NBu₄]₆H[PMo₂W₉O₃₉] molar ratios in DMSO, C_{Er(III)} = 0.001 mol/l.

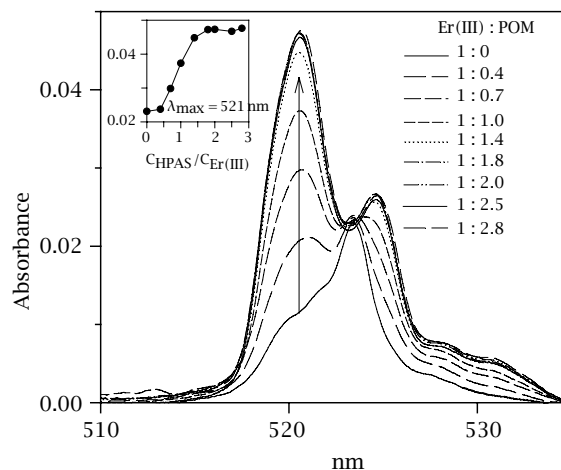


Figure 2. Absorption spectra of Er(III) in the range of the hypersensitive transition ($^4I_{15/2} \rightarrow ^2H_{11/2}$) for various Er : [NBu₄]₆H[PMo₂W₉O₃₉] molar ratios in DMF, C_{Er(III)} = 0.001 mol/l.

These spectra show an increase in absorption and a shift of their maxima consistent with formation of ML₂ complexes.

Recently, based on the analyses of the absorption spectra of Nd(III) and Er(III) ions, we evidenced formation of the ML and ML₂ complexes with Keggin's and Dawson's type of polyanions [7, 18, 26] and ML complexes with the polyanion [(Na)As₄W₄₀O₁₄₀]²⁷⁻ [18] in aqueous solutions. In the case of [MnMo₉O₃₂]⁶⁻

(Anderson's anion) with the Nd(III) ion spectroscopic studies demonstrated that the M_2L type of complexes occur in solution [7].

Formation of the ML_2 sandwiched complexes in non-aqueous solvents (DMSO, DMF, acetonitrile) as are shown in Figures 1 and 2. They were also earlier observed in aqueous solutions [7, 26]. Our studies concerning chemometrics and factor analysis of the Nd(III) absorption spectra with chosen POM complexes confirmed formation of the M_2L , ML , ML_2 complexes [26, 27]. In spectrophotometric studies we also proved that formation of $LnPOM$ complexes is function of ionic strength. For example, in equimolar solutions of Nd(III) and Keggin's POM of high ionic strength, a preferential formation of the sandwich complexes $Nd(HPAS)_2$, instead of $NdHPAS$, were observed [6, 7].

Eu(III) luminescence studies (intensity, lifetime measurements and quantum yield) of the EuPOM systems were used to investigate their emission properties, effectiveness of energy transfer processes, hydration numbers and complex compositions [6, 7].

The Eu(III) luminescence lifetimes measured for the Eu/POM complexes were used to calculate the number of water molecules present in the inner sphere of the Eu(III) ion, using the following eq. [28]:

$$n_{H_2O} = 1.05\tau_{H_2O}^{-1} - 0.7 \quad (2)$$

The lifetime of Eu(III) excited state is efficiently quenched by OH oscillators of inner sphere H_2O molecules bound to the Eu(III) ion. Based on the Eu(III) luminescence lifetime measured for EuPOM complexes in non-aqueous solutions and solid the hydration numbers of this ion were calculated as shown in Table 1 and compared with those obtained earlier in aqueous solution [5–7]. The measured Eu(III) luminescence lifetime gave the longest values for sandwiched complexes with inorganic counter cations in aqueous solution (from 1.2 to 3.5 ms) and with organic counter cation (1.11 ms) in DMF solution. The hydration numbers calculated from the measured lifetime values indicate no water molecules in the Eu(III) inner coordination sphere of the complexes. In the case of Eu(III) encapsulated Preyssler's complexes, the composition with organic counter ion $(NBu_4)_{12}[(Eu)P_5W_{30}O_{110}]$ has smaller hydration number (~ 0.5) than that with inorganic counter ion $K_{12}[(Eu)P_5W_{30}O_{110}]$ having 3 waters of hydration. It is worth to mention that the solid Eu(III) complexes have coordination number of 8 or 9 in the case of solution.

Examples of the luminescence excitation and emission spectra of Eu/POM complexes recorded in non-aqueous solvents are presented in Figure 3.

The Eu(III) luminescence lifetimes obtained for Eu/POMs in non-aqueous solvents with various molar ratios of the components demonstrated the ML_2 complex formation (see Figure 4).

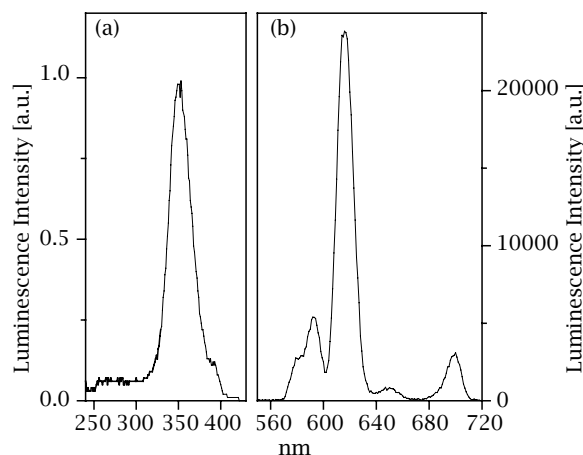


Figure 3. Luminescence excitation (a) and emission (b) spectra of Eu(III) in $(NBu_4)_8H_3[Eu(PMo_2W_9O_{39})_2]$ in DMF.

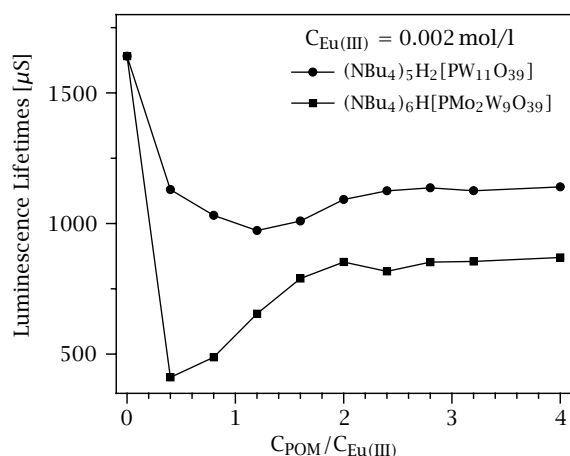


Figure 4. Eu(III) luminescence lifetime as a function of the POM : Eu(III) molar ratios in non-aqueous solvent (DMF).

The luminescence spectra of non-aqueous solutions are generally similar to those obtained in aqueous solution [6]. Excitation spectra of the Eu(III) molibdotungstate compounds show strong emission band ($\lambda_{max} \sim 340$ nm) due to ligand to metal energy transfer (LMET) from the tungstate group to the Eu(III) ion [29, 30].

Our previous studies have shown that the most intense Eu(III) luminescence was observed for the $(EuW_{10}O_{36})^{9-}$ and $[Eu(SiMoW_{10}O_{39})_2]^{13-}$ sandwiched complexes due to energy transfer from the tungstate group to the Eu(III) ion. In the case of $[Eu(SiW_{11}O_{39})_2]^{13-}$ and $[Eu(P_2W_{17}O_{61})_2]^{17-}$ and the Eu-encrypted complexes a weak luminescence intensity was observed. In latter cases the transfer from ligand to Eu(III) does not occur. Interesting pattern of the Eu(III) luminescence lifetime and quantum yield were observed in the case of the heterotungstomolybdate Eu-sandwiched complexes $\{[Eu(Si(P)Mo_xW_{11-x}O_{39})_2]^{13-}\}$. A linear dependence

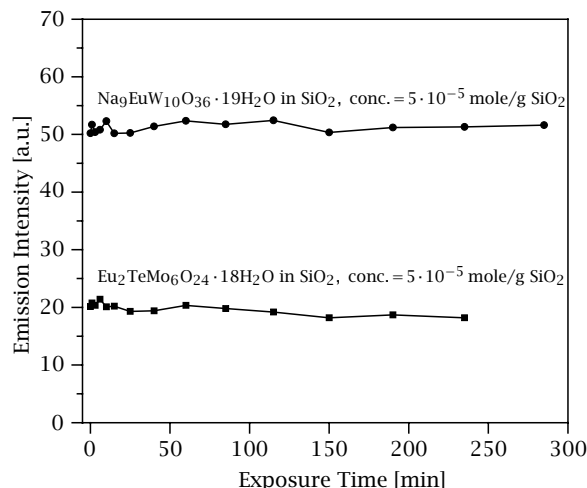


Figure 5. The photochemical stability of EuPOMs complexes.

of the Eu(III) luminescence lifetime, τ , and quantum yield, ϕ , on the content of Mo (number of atoms x , where $x = 0-9$) in the $[\text{Eu}(\text{Si}(\text{P})\text{Mo}_x\text{W}_{11-x}\text{O}_{39})_2]^{13-}$ structures were observed. These dependences can be applied for the determination contents of Mo in polytungstomolybdate complexes [6, 9, 18].

Based on luminescence lifetimes measured both for solid and aqueous solutions, we found no H_2O in Eu(III) inner sphere in the sandwiched complexes $\text{Eu}(\text{POM})_2$. Whereas the complexes Eu_2POM have four or six water molecules and europium-encrypted derivatives possess three or four H_2O 's in the Eu(III) inner coordination sphere.

In order to increase photochemical stability and to minimise water (O – H oscillators) interaction, we used Eu(III) complexes with the heteropolyanions ($\text{Na}_9\text{EuW}_{10}\text{O}_{36}$, $\text{Eu}_2\text{TeMo}_6\text{O}_{24}$) entrapped in silica xerogel matrix. The luminescence characterization of EuPOM complexes entrapped to xerogels are presented in Table 2. The resulting encapsulation and immobilization of Eu(III) complexes with POMs in xerogel matrices enhanced emission intensities and luminescence quantum yield related to solid EuPOM and EuPOM dissolved in the solutions.

The Eu(III) complexes entrapped in xerogels were tested for their photochemical stability during UV irradiation. As it is shown in Figure 5, the emission intensity (at $\lambda_{\text{max}} = 617 \text{ nm}$, when $\lambda_{\text{exc}} = 273 \text{ nm}$) of the silica xerogel doped with Eu(III) complexes during UV irradiation remains constant within experimental error. Thus, for the Eu(III) in inorganic environment there is present no photodegradation effect due to relative high energy (UV) quanta used for the irradiation.

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