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Spectroscopic studies of Eu(III) and Nd(III) complexes with several polyoxometalates

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Abstract

The results of studies related to synthesis and spectroscopic properties of polyoxometalates (POM) and their europium(III) and neodymium(III) complexes (Ln/POM) are presented. A series of lanthanide(III) sandwiched $Ln(POM)_2$, Ln_2POM or encapsulated within the cavity of the POM complexes, synthesized for these studies, were verified based on the results of thermogravimetric analysis and infrared spectroscopy. Absorption of Nd(III) and luminescence (excitation and emission) spectra of Eu(III) as well as results of Eu(III) ion lifetime measurements were used for characterization of the complexes. The Eu(III) luminescence lifetimes, measured both for solid and aqueous solutions, indicate that the sandwiched complexes $Eu(POM)_2$ have no water of hydration, whereas the complexes Eu_2POM have four or six water molecules, and europium-encrypted derivatives three or four H_2Os in the Eu(III) inner coordination sphere.

Keywords: Polyoxometalates; Eu(III) and Nd(III) complexes; Absorption and luminescence spectra; Luminescence lifetimes

1. Introduction

The photochemistry of polyoxometalates is a great interest to inorganic chemists. Papers dealing with luminescence processes occurring in lanthanide polyoxometalate ions Ln/POM occupy an important position [1–5]. Lanthanide(III) ions, with their large ionic radii and high charge densities, form $Ln(POM)_2$ complexes in which the lanthanide is sandwiched between the defect site of two ligands. The Ln(III) ions can be encapsulated selectively by heteropolytungstate anions such as: $[(Na)P_5W_{30}O_{110}]^{14-}$, $[(Na)Sb_9W_{21}O_{86}]^{18-}$ and $[(K)As_4W_{40}O_{140}]^{27-}$ that act as inorganic cryptands [6–8]. The photoexcitation of the oxygen-to-metal charge transfer (O–M lmct) bands of the polyoxometalloeuropates of W and Mo induces Eu(III) emission as a result of the intramolecular energy transfer to the emitting $^5D_0$ state of Eu(III) ion [5,9–11]. A variety of the luminescent Eu/POM ions have been used to study the coordination geometry of Eu(III) and its emission properties such as spectrum, lifetime and energy transfer. In our previous paper the luminescence spectra and lifetime of Eu(III) in the europium-encrypted Preyssler heteropolyanion $[EuP_5W_{30}O_{110}]^{12-}$ have been studied [12].

In this work we report a study of the Nd(III) absorption and Eu(III) luminescence when these cations are complexed with various POM ligands. The absorption spectra of Nd(III), in the hypersensitive transition range, and the Eu(III) luminescence (excitation and emission) spectra, luminescence lifetimes and luminescence quantum yield of the Eu(III) ion were measured for spectroscopic characterization of a series of Ln(III): sandwiched $Ln(POM)_2$, encapsulated within the cavity of the POM and Ln_2POM complexes.

2. Experimental

2.1. Synthesis of compounds

The POMs and their Eu(III) complexes were prepared according to previously published methods.The heteropolytungstates $K_8SiW_{11}O_{39}\cdot 17H_2O$ (I), $K_{8(7)}Si(P)W_{11x}Mo_xO_{39}\cdot 17H_2O$ (II), $K_{10}P_2W_{17}O_{61}\cdot 27H_2O$ (III), and Eu(III)-sandwiched complexes: $Na_9EuW_{10}O_{36}\cdot 19H_2O$ (IV), $K_{13}[Eu(SiW_{11}O_{39})_2]\cdot 16H_2O$ (V), $K_{13}[Eu(SiW_{11x}Mo_xO_{39})_2]\cdot 28H_2O$ (VI), and $K_{17}[Eu(P_2W_{17}O_{61})_2]\cdot 32H_2O$ (VII) were prepared as described earlier [10–14]. The inorganic cryptands $K_{12\ 5}Na_{1.5}[(Na)P_5W_{30}O_{110}]\cdot 22H_2O$ (VIII), $(NH_4)_{18}[(Na)Sb_9W_{21}O_{86}]\cdot 24H_2O$ (IX) and

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$Na_{27}[(K)As_4W_{40}O_{140}]\cdot 71H_2O$ (X) were synthesized and purified according to the published procedures [12,13,15]. The general formation process is a condensation of monomeric oxoanions (i.e. WO_4^{2-}, and PO_4^{3-}, AsO_2^- or Sb_2O_3) in acidic aqueous solution, governed by reaction conditions, notably pH, ratio of reactants and temperature. The Eu-encrypted derivatives: $K_{12}[(Eu)P_5W_{30}O_{110}]\cdot 54H_2O$ (XI), $(NH_4)_{16}[(Eu)Sb_9W_{21}O_{86}]\cdot 40H_2O$ (XII) and $K_{25}[(Eu)As_4W_{40}O_{140}]\cdot 39H_2O$ (XIII) were synthesized for these studies as described in [12,16–18]. The compositions of Eu:POM=2:1 of the following formulae $Eu_2TeMo_6O_{24}\cdot 17H_2O$ (XIV) and $[Eu_2CeMo_{12}O_{42}]^{2-}$ (XV) were obtained from $(TeMo_6O_{24})$ (XVI) [19] and $(CeMo_{12}O_{42})^{8-}$ (XVII) [20,21], as described in [22,23]. The polyoxomatalate $(NH_4)_6MnMo_9O_{32}\cdot 6H_2O$ (XVIII) was prepared according to the previously described method [24].

Identification was done by comparison of the IR spectra of obtained compounds with those previously reported, thermogravimetric analysis and spectrophotometric determination of W(VI) and Mo(VI) contents. Contents of tungsten and molybdenum in heteropolyanions studied were determined with the use of a new spectrophotometric procedure for the simultaneous determination of molybdenum and tungstate with disodium-1,2-dihydrobenzene-3,5-disulfonate (Tiron) [25].

2.2. Methods

The IR spectra were obtained by means of an FTIR Bruker IFS 113v spectrophotometer, and the samples were prepared in KBr. The absorption spectra were recorded by means of a UV-2401PC Shimadzu spectrophotometer. Nd(III) spectra in the hypersensitive transition $^4I_{9/2}\rightarrow{}^2H_{9/2}$ were measured in the range of 775–830 nm in 5-cm glass cells. The corrected luminescence spectra of Eu(III) were recorded using a Perkin-Elmer MPF-3 spectrofluorimeter (λ_{exc} were ~300 (lmct), 394 or 464 nm). The luminescence lifetime measurements were carried out using the detection system consisted of a nitrogen laser (KB6211) and a tunable dye laser [26]. The luminescence decay curves observed in this work were analyzed by a single exponential relation, providing the decay constants ($k=\tau^{-1}$).

3. Results and discussion

Representatives of POMs, categorized into three structural groups, having tetrahedrally (I–VII), octahedrally (XIV, XVI, XVIII) and icosahedrally (XV, XVII) coordinated central core, and compositions that encapsulate lanthanides (XI–XIII) have been chosen for these studies. FTIR spectra (peak positions, shapes and relative intensities) for these POMs and their complexes with Ln(III) ions were used to characterize the compositions and to fingerprint the structures in solution. The complexes of these POMs with lanthanide(III) ions were characterized using Nd(III) absorption spectra of the hypersensitive band at ~796 nm and Eu(III) luminescence spectra and lifetime measurements.

Nd(III) absorption spectra of hypersensitive transition $^4I_{9/2}\rightarrow{}^2H_{9/2}$, which maximum and intensity are sensitive to ligand field of POMs, allow to evaluate the formation of Nd/POM complexes. Examples of the Nd(III) absorption spectra of the hypersensitive transition $^4I_{9/2}\rightarrow{}^2H_{9/2}$ measured for various Nd(III):POM ratio and as a function of ionic strength of solution, are presented in Fig. 1(a–c). Absorption spectra of Nd(III) in the sandwiched complex $Nd(POM)_2$ with the Dawson type of POM (VII) (i.e. $Nd(P_2W_{17}O_{61})_2^{17-}$) as a function of metal:ligand ratio ranging from 1:0.5 to 1:3 are presented in Fig. 1a. The spectra show the vanishing of the uncomplexed Nd(III) ion with an absorption band at 794.1 nm and formation of the NdPOM, with an absorption band at 801.6 nm, and $Nd(POM)_2$ complexes with absorption bands at 802.7 nm and 808.9 nm, as the Nd:POM molar ratio increases.

Fig. 1b presents a formation of Nd_2POM (with λ_{max} at 796.5 nm), based on absorption measurements for isomolar solutions of Nd:POM (XVIII), in which the total concentration of the components was kept at 0.002 mol/l.

In Fig. 1c are shown absorption spectra of the Nd(III):$PMoW_{10}O_{39}^{7-}=1:1$ system, as a function of ionic strength. An increase of (KCl concentration) ionic strength, $I\geq 0.5$, causes a formation of new bands with λ_{max} at 803.2 and 809.4 nm characteristic for the sandwiched $Nd(POM)_2$ complex. At the same time an increase of absorption band with λ_{max} at 794.3 nm, characteristic for the uncomplexed Nd(III) ion, and a decrease of absorption for the characteristic band of the 1:1 complex, with λ_{max} at 801.5 nm, is observed.

Examples of the luminescence excitation and emission spectra of Eu/POM complexes in aqueous media and solid are shown in Figs. 2 and 3.

The most intense Eu(III) luminescence (solid and in water solution) was observed for the $(EuW_{10}O_{36})^{9-}$ and $[Eu(SiW_{10}MoO_{39})_2]^{13-}$ sandwiched complexes and for $Eu_2TeMo_6O_{24}$ due to energy transfer from the tungstate group to the Eu(III) ion [9–11]. The luminescence excitation and UV–Vis absorption spectra show the intense broad of the oxygen-to-metal charge transfer (O–M) LMCT bands (with max. 250–360 nm) (Fig. 2 and Fig. 3). The Eu(III) luminescence intensity, I_{lum}, of other sandwiched complexes indicates a decrease of the efficiency of the energy transfer from polytungstate group to the Eu(III) in the $[Eu(SiW_{11x}Mo_xO_{39})_2]^{13-}$ polyanions as x increases. In the case of $[Eu(SiW_{11}O_{39})_2]^{13}$ and $[Eu(P_2W_{17}O_{61})_2]^{17-}$ a weaker luminescence intensity is observed. In theses cases the transfer from ligand to Eu(III) does not occur and no bands in the excitation spectra in the UV region were observed.

In the case of Eu(III) sandwiched complexes the Eu(III)

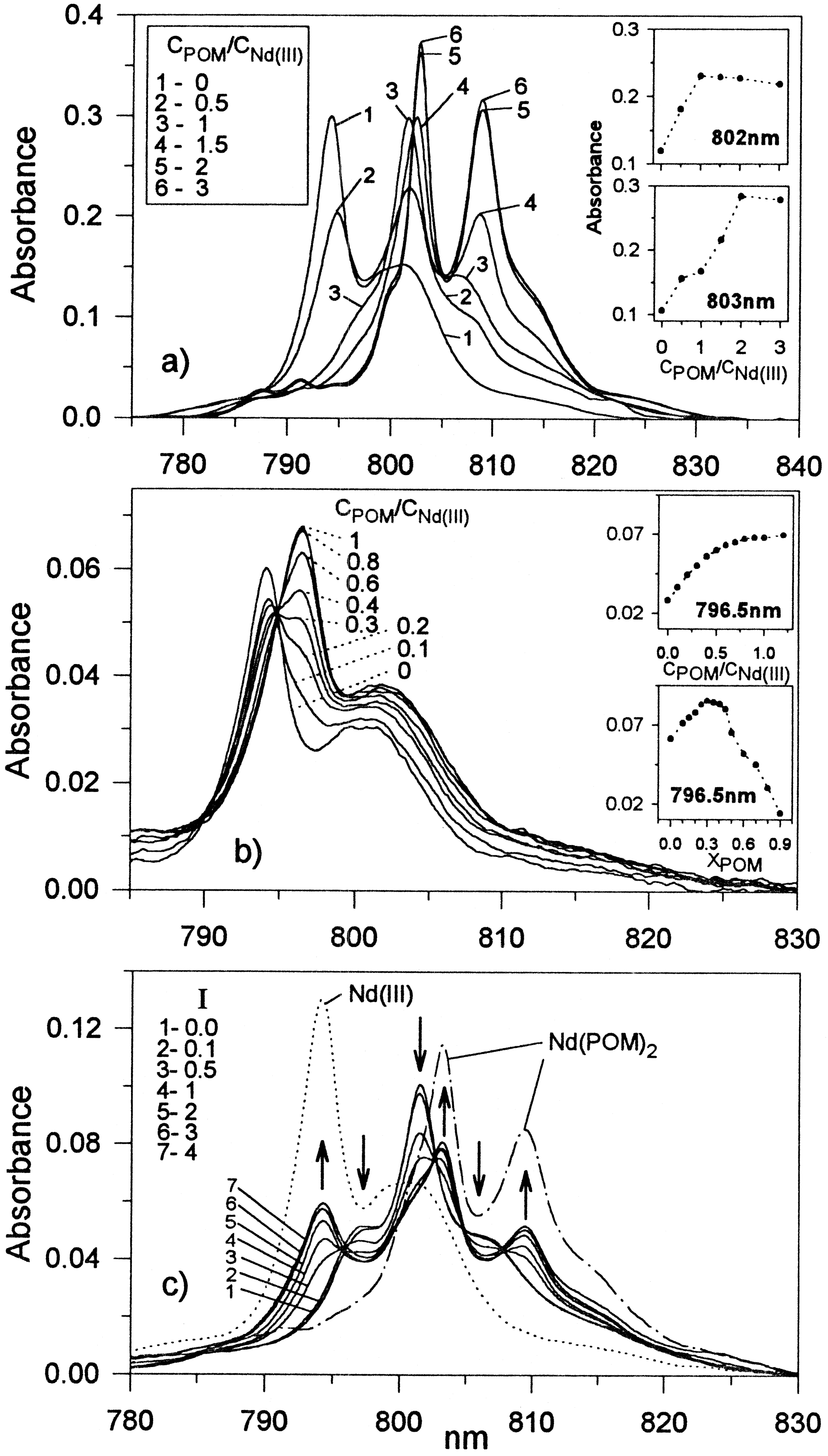

Fig. 1. Nd(III) absorption spectra of the $^4I_{9/2} \rightarrow {}^4H_{9/2}$ hypersensitive transition: as a function of various $[P_2W_{17}O_{61}^{10-}]$/[Nd(III)] molar ratio (a), in isomolar solutions of $[MnMo_9O_{32}^{6-}]$:[Nd] with the total component concentration = 0.002 mol/l (b), and as a function of ionic strength of [Nd(III)]:$[PMoW_{10}O_{61}^{7-}]$ = 1:1 complex solution (c).

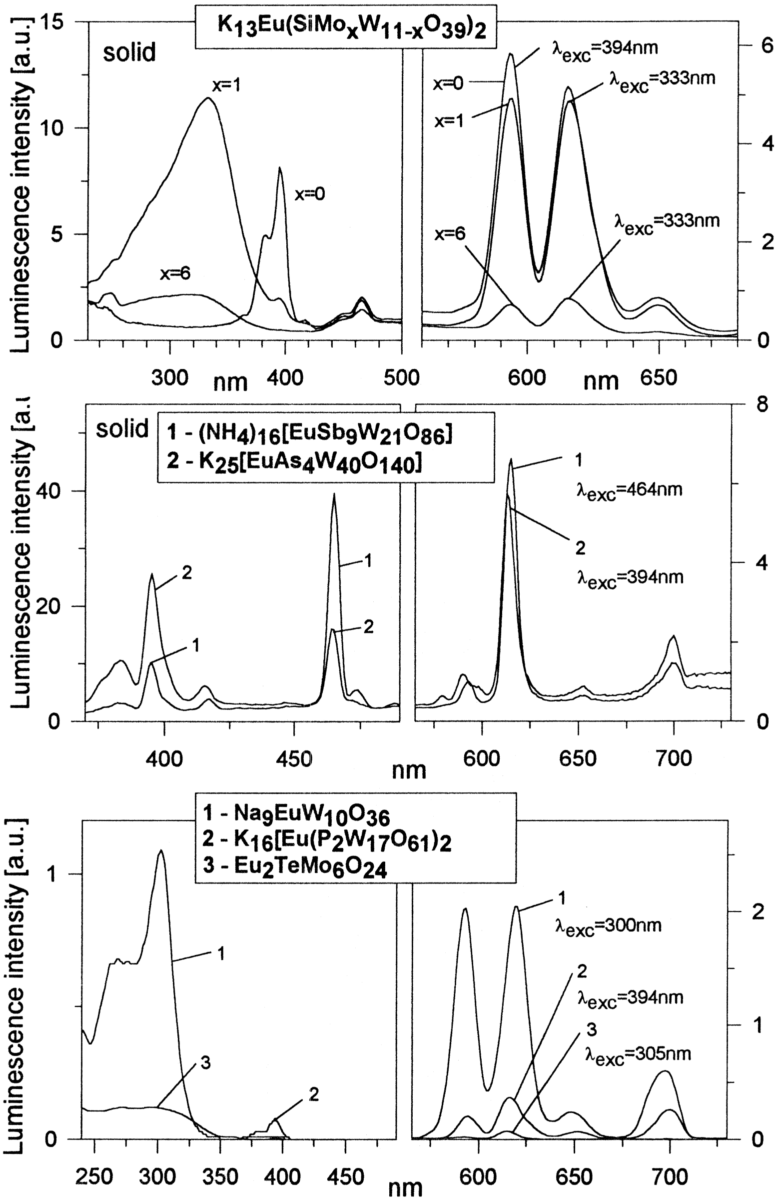

Fig. 2. Luminescence excitation (left) and emission (right) spectra of chosen Eu/POM complexes in solid and water solution.

luminescence intensity in aqueous solution strongly depends on the ionic strength, *I*. The I_{lum} increases as *I* increases (Fig. 4).

The Eu(III) emission spectrum shows two most intense bands at 594 and 615 nm, associated with $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ (exhibiting hypersensivity) transitions. Table 1 presents the values of the relative integral intensities (ratio of $\eta = I_{615}/I_{594}$) which are sensitive to the primary coordination sphere about the Eu(III) ion. The I_{lum} of the Eu(III) aqua ion ($Eu(H_2O)_9^{3+}$) at 615 nm is weaker than that at 594 nm ($\eta = 0.3$) and in the case of Eu/POM complexes the ratio η is higher, indicating lower symmetry of Eu(III) complexes than the aqua ion. Calculated values of η are presented in Table 1, together with Eu(III) luminescence lifetimes and its hydration numbers in complexes studied. Calculated η values (1.1 for $[(Eu)P_5W_{30}O_{110}]^{12-}$, 5.4 for $[(Eu)Sb_9W_{21}O_{86}]^{18-}$, 3.9 for $[(Eu)As_4W_{40}O_{140}]^{27-}$ and 0.8 ($x=0$)−1.6($x=9$) for solid $[Eu(SiWi_{11x}Mo_xO_{39})_2]^{13-}$) show the highest symmetry in the case of $[(Eu)P_5W_{30}O_{110}]^{12-}$ and $[Eu(SiW_{11x}Mo_xO_{39})_2]^{13-}$ complexes. Also higher symmetry of the EuPOM complexes in solid is observed. Higher symmetry of complexes in the solid state (lower values of $\eta = (I_{615}/I_{594})$ rather than in solution is a result of a restraint of oscillations and a lack of interactions with solvent).

The Eu(III) luminescence lifetimes measured for the solid and their solutions (H_2O and D_2O), as shown in Table 1, were used to calculate the number of water

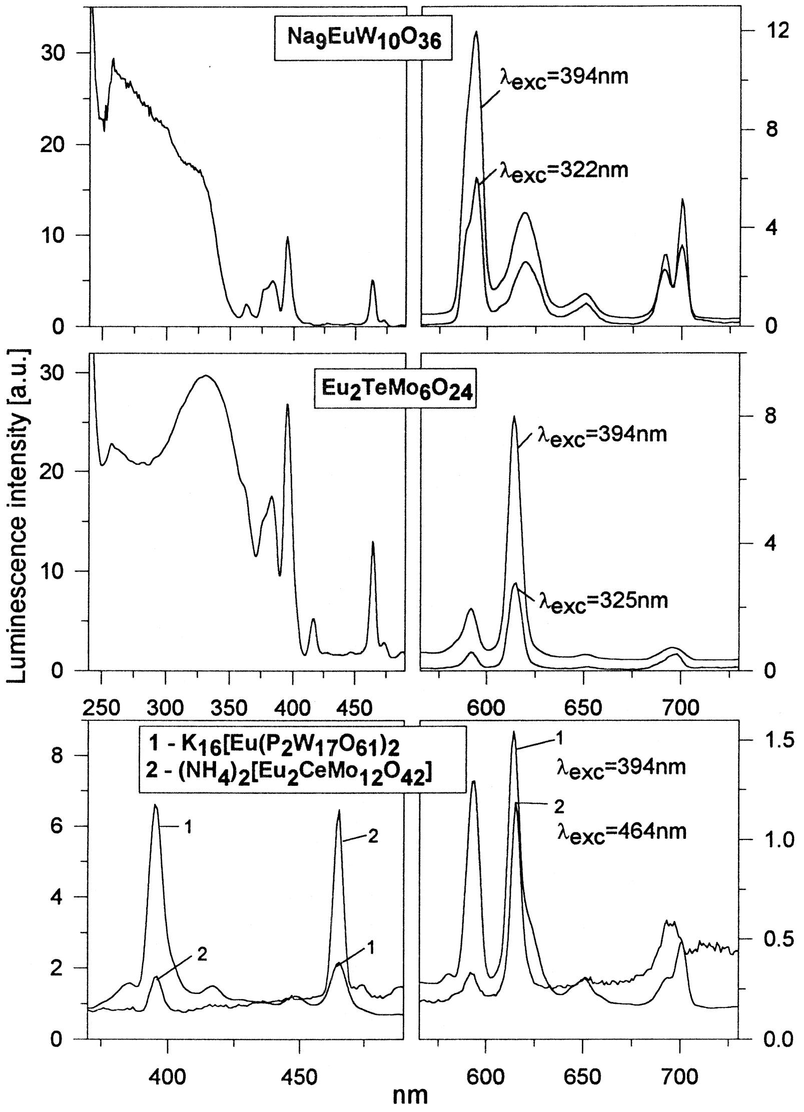

Fig. 3. Luminescence excitation (left) and emission (right) spectra of chosen Eu/POM complexes in solid.

molecule bonds in the inner sphere of the Eu(III) ion from the equations. below [27,28]:

$$n_{H_2O} = 1.05\,(\tau^{-1}_{H_2O} - \tau^{-1}_{D_2O})$$

$$n_{H_2O} = 1.05\,\tau^{-1}_{H_2O} - 0.7$$

The decay rate ($k=1/\tau$) of the $^5D_0 \rightarrow {}^7F_j$ emission increased with increasing number of aqua ligands coordinating the Eu(III) ion due to the weak vibronic coupling of the $^5D_0$ excited state with vibrational states of the high frequency OH oscillators of the aqua ligands [29].

Eu(III) luminescence lifetimes (Table 1), measured both for solid and aqueous (H_2O and D_2O) solutions, indicate that the sandwiched complexes have no water of hydration, whereas europium-encrypted derivatives have three (solid) or four (solution) water molecules and the Eu/POM=2:1 complexes have four to six water molecules in the Eu(III) inner coordination sphere. The hydration number of Eu(III) was calculated in the Eu(III):$PMoW_{10}O_{39}^{7-}$ =1:1 system, as function of ionic strength. The calculated n_{H_2O} value in solutions at a high ionic strength, $I \geq 2$, indicates a formation of the sandwiched $Eu(POM)_2$ complex with no water of hydration, whereas in solutions at low ionic strength the existing complex 1:1 ($EuPMoW_{10}O_{39}^{7-}$) has four water molecules in the Eu(III) inner coordination sphere. This observation confirms the conclusion obtained from the Nd(III) absorption spectra. In solution, the complex $[Eu_2TeMo_{12}O_{42}]^{2-}$ has a hydration number 5 which is lower than in the solid (6), this can indicate its polymeric structure in solution [23].

An interesting pattern of the Eu(III) luminescence

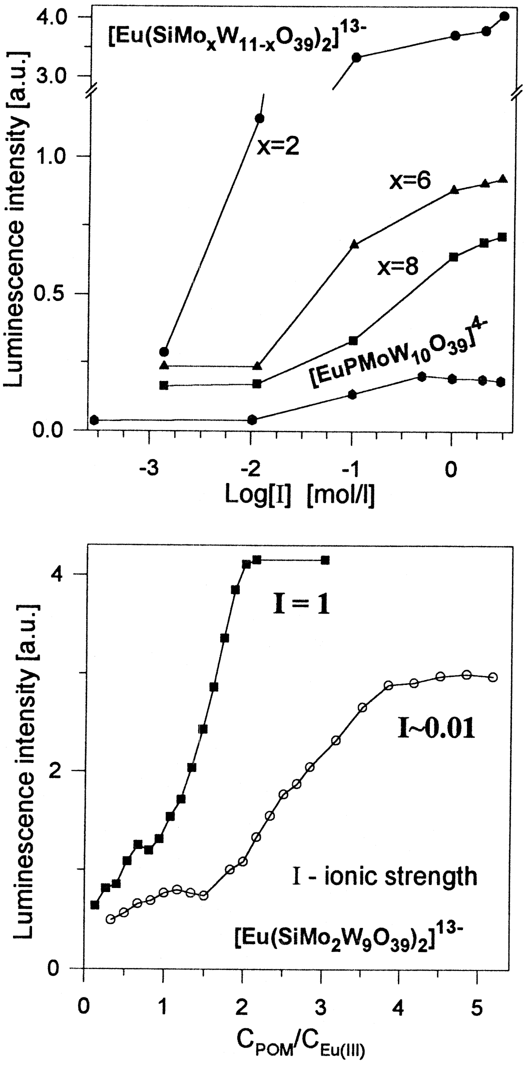

Fig. 4. Dependence of the Eu^{3+} luminescence intensity of $[Eu(SiW_{11-x}Mo_xO_{39})_2]^{13-}$ complexes on ionic strength in aqueous solution..

intensity and quantum yield of the Eu(III) luminescence was observed in the case of the heterotungstomolybdate Eu-sandwiched complexes $\{[Eu(SiW_{11x}Mo_xO_{39})_2]^{13-}\}$ [30]. A linear dependence of the Eu(III) luminescence quantum yield, ϕ, on the number of Mo atoms, x, in these structures was obtained. Similarly, a linear dependence of the luminescence lifetime of the Eu(III) ion, τ, on the content of Mo (number of atoms x, where $x=0$–9) in the $[Eu(SiW_{11x}Mo_xO_{39})_2]^{13}$ compositions was recently observed [31].

Acknowledgements

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Table 1
Luminescence data and calculated hydration numbers of the Eu/POM complexes

Composition	$^{\lambda}$exc	I_{615}/I_{595}	τ [ms]		n_{H_2O}
Solid					
$[EuW_{10}O_{36}]^{9-}$	322	0.3			
	394	0.4	3.18		0
$[Eu(SiW_{11}O_{39})_2]^{13-}$	394	0.9	2.43		0
$[Eu(SiMo_6W_5O_{39})_2]^{13-}$	333	1.2			
	394		1.72		0
$[Eu(P_2W_{17}O_{61})_2]^{17-}$	394	1.2	2.13		0
$[EuP_5W_{30}O_{110}]^{12-}$	394	–	0.30		3
$[EuAs_4W_{40}O_{140}]^{25-}$	394	3.9	0.26		3
$[EuSb_9W_{21}O_{86}]^{16-}$	394		0.27		3
	464	5.4			
$Eu_2TeMo_6O_{24}$	325	3.8			
	394	4.1	0.16		6
$[Eu_2CeMo_{12}O_{42}]^{2-}$	394		0.22		4
	464	2.9			
Solution			*H_2O*	*D_2O*	
$[EuW_{10}O_{36}]^{9-}$	300	1.0			
	394		2.29	4.32	0
$[Eu(SiW_{11}O_{39})_2]^{13-}$	394	1.1	3.46	5.38	0
$[Eu(SiMo_6W_5O_{39})_2]^{13-}$	342	1.5			
	394		2.59	3.54	0
$Eu(P_2W_{17}O_{61})_2]^{17-}$	394	1.8	3.08	4.76	0
$[EuP_2W_{30}O_{110}p]^{12-}$	394	1.1	0.32	5.03	3
$[EuAs_4W_{40}O_{140}]^{25-}$	394	4.3	0.25	2.21	4
$[EuSb_9W_{21}O_{86}]^{16-}$	394	–	0.22	1.35	4
$Eu_2TeMo_6O_{24}$	305	3.9			
	394		0.19	1.15	5
$[Eu_2CeMo_{12}O_{42}]^{2-}$	394	–	0.21	0.96	4

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