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Spectroscopic characterization of chosen Ln(III) polyoxometalate complexes with organic counter cations in solid and in non-aqueous solutions

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Abstract

Polyoxometalate (POM) compositions containing organic counter cations and $SiMo_2W_9O_{39}{}^{8-}$ polyanion have been synthesized using extraction. Several compounds with counter ions containing phosphorus such as: $Ph_3P^+CPh_3$, Ph_3P^+Et, $Ph_3P^+C_{16}H_{33}$, Ph_4P^+, Bu_4P^+ were obtained and their Eu(III) complexes synthesized. Luminescence characterization of the europium complexes concerning their intensities, quantum yields and luminescence lifetimes of Eu(III) ion both in DMF solutions and solid are discussed. The complexation study has been carried out analyzing absorption spectra of Nd(III) ion in the range of its hypersensitive transition ($^4I_{9/2} \rightarrow {}^2H_{9/2}$). Results indicated formation of the $Ln(POM)_2$ sandwich complexes. Computer-assisted target factor analysis has been applied to evaluate the spectra of Nd(III) in DMSO solutions containing varying amounts of the POM. The conditional formation constants with $\lg \beta_{12} = 8.6 \pm 0.5$, $\lg \beta_{12} = 8.2 \pm 0.4$ and $\lg \beta_{12} = 9.6 \pm 0.7$ were obtained for $(Ph_3PEt)_5H_3SiMo_2W_9O_{39}$, $(Ph_3PC_{16}H_{33})_7HSiMo_2W_9O_{39}$ and $(Ph_3PCPh_3)_6H_3SiMo_2W_9O_{39}$, respectively. Studies have shown significant influence of the counter ion structure on the luminescence properties of Eu(III) in the systems studied. The most intensive luminescence and the highest value of quantum yield were observed in the case of the complex $(Ph_3PCPh_3)_7H_6Eu(SiMo_2W_9O_{36})_2$, containing six phenyl groups in the organic counter cation.

Keywords: Polyoxometalates; Ln(III) complexes; Non-aqueous solutions; Eu(III) luminescence

1. Introduction

Polyoxometalate (POM) compounds, particularly the most known compositions named Keggin's type ($[XW_{11}O_{39}]^{7,8-}$ (X-P(V), Si(IV))), have received much attention because of their wide applications in different fields of chemistry and medicine [1–4]. These compounds are even more interesting as they form complexes with transition metal ions (mainly d- or f-elements), due to their applications in many areas. In the last decade different synthetic approaches have been used to incorporate organic or organometallic moieties in polyoxoanion frameworks [5]. Detailed solution studies of POMs have been carried out, especially in aqueous media, using various methods, in particular spectroscopic and electrochemical techniques. In the case of POM complexes with lanthanide(III) ions, Ln(III), in aqueous media strong quenching of emission processes is observed as well as significant pH influence on solution equilibria occurs [6]. In non-aqueous solutions quenching processes of the lanthanide(III) ion luminescence are considerably reduced by eliminating of the O–H oscillators from water molecules and as a result stronger emission is observed [7].

Our previous studies concerned the Keggin's type of polyoxoanions and their Ln(III) complexes in water solution and in solid [8–13] and most recently we concentrated our attention on polyoxometalate complexes with organic counter anions [14].

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This paper shows results obtained for the $SiMo_2W_9O_{39}{}^{8-}$ anion and its Eu(III) complexes with various counter cations RP^+ ($Ph_3P^+CPh_3$, Ph_3P^+Et, $Ph_3P^+C_{16}H_{33}$, Ph_4P^+, Bu_4P^+) soluble in non-aqueous media (DMF, DMSO, acetonitryle). Spectroscopic characterization of the Eu(III) complexes in this form, as solid and in non-aqueous solutions is presented.

2. Experimental

2.1. Synthesis of compounds

All reagents used in these studies were at least analar grade, Eu_2O_3 and Nd_2O_3 spectroscopically pure and non-aqueous solvents (DMF, DMSO, acetonitrile, dichloromethane) pure for UV spectroscopy (Fluka, Aldrich). Potassium salt of the POM studied was synthesized and characterized as published earlier [10]. The salts with organic counter cations RP^+ were obtained using the modified procedure [15] developed by Lyon et al. [16].

2.1.1. Synthesis of RPPOM salts

The potassium salt of POM (0.5 mmol) was dissolved with stirring in water (250 ml) to form a clear solution. The pH was adjusted to 5.0–5.2 with sulfuric acid (0.18 mol/l). Four millimoles of RPCl or RPBr salts was added slowly while the pH was maintained in the range 6–7 with sulfuric acid (0.18 mol/l). The resulting white cloudy solution was extracted with acetonitryle (17 ml) and dichloromethane (34 ml) by shaking for 5 min. The clear organic layer was slowly evaporated to dryness. The product was dissolved in dichloromethane and small amounts of acetonitryle solvents and then diethyl ether (10–20 ml) was added resulting in the precipitation of solid. The solid was filtered off and dried in vacuum. The obtained compound was recrystallized from acetonitrile.

2.1.2. Synthesis of RP-EuPOM salts

The RP salts of Eu(III)POM complexes (RPEuPOM) were obtained by mixing of 5 ml of Eu(III) acetonitrile solution (0.004 mol/l) and RP-POM (solid, 4×10^{-5} mol) and 5 ml of DMF to give 10 ml of clear mixture (Eu:POM 1:2). This solution was stirred for 1 h in 50 °C. The product was isolated by adding 10 ml of ether and dried in vacuum. Solid compounds were recrystallized from acetonitrile with addition of ether and dried in vacuum.

2.2. Methods

Elemental analysis was made on an Elemental analyzer model VARIO ELIII. Molybdenum and tungsten determination [17] was made after previous 2 h calcinations of sample at 700 °C and dissolved in 2 ml of NaOH solution (1 mol/l). Thermogravimetric analysis was conducted using a SETARAM SETSYS TG-DSC 15 system. The conditions of measurements were as follows: temperature interval 20–550 °C, heating rate: 2 °C/min, specimen weight: ∼8–12 mg, air flux: 1.9 l/h; $CuSO_4{\cdot}3H_2O$ was used as a reference material. The IR spectra were obtained by means of a FTIR Bruker IFS 113v spectrophotometer, and the samples (∼2 mg) were prepared in KBr. The absorption spectra were recorded using a UV-2401PC Shimadzu spectrophotometer. The corrected luminescence spectra of Eu(III) ion were recorded using a Perkin-Elmer MPF-3 spectrofluorimeter. The luminescence lifetime measurements were carried out using the detection system consisted of a nitrogen laser (KB6211) and a tunable dye laser [18].

The luminescence quantum yield, Φ, of the Eu(III) ion in solution was calculated using $[Ru(bpy)_3]Cl_2$ as a standard. In the case of powder samples Φ was determined as we described earlier [19] based on the procedure described by Wrighton et al. [20] from Eq. (1):

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

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 (KBr) and samples, respectively, at the excitation wavelength.

3. Results and discussion

Polyoxometalates compositions containing organic counter cations, tetrabutylphosphonium analogs ($Ph_6 = Ph_3P^+CPh_3$, $Ph_3Et = Ph_3P^+Et$, $Ph_3C_{16} = Ph_3P^+C_{16}H_{33}$, $TPP = Ph_4P^+$, $TBP = Bu_4P^+$) and $SiMo_2W_9O_{39}{}^{8-}$ ($SiMo_2W_9$) polyanion have been synthesized using extraction [13,14]. $SiMo_2W_9O_{39}{}^{8-}$ was selected for this study due to its high luminescence intensity, resulting from oxygen-to-metal charge transfer (O–M) LMCT bands (with maximum 250–360 nm) observed in our previous luminescence studies of Eu(III) complexes [9,11]. Identification of obtained compounds was done with the use of a combination of elemental analysis (Table 1), thermogravimetric (Fig. 1) analysis and comparison of the IR spectra (Fig. 2) with those previously reported for potassium salts [9,10,20–23].

The examples of thermogravimetric curves (TG and DTG as first derivative of TG curve and DTA analysis) are shown in Fig. 1. The observed DTA curves shows a strong exothermic signal in the range of 400–500 °C corresponding to the weight loss of an organic material, i.e., RP^+ cations as $(RP)_2O$. This effect can be assigned to combustion of the sample (analysis has been carried out in the air). In the range up to 130 °C only a small weight loss is observed, based on which the number of crystallization water molecules has been calculated.

Elemental analysis in some cases is unreliable for formulations of polyoxoanion compositions [15]. In such this case, the IR and thermogravimetric analysis as complementary methods to the elemental analysis of POM's are applied and on the basis of these three methods it was possible to

Table 1
Analytical data for RPPOM and RPEuPOM salts

Compound	Elemental (%)				TG ($\Delta m_{55\,^{\circ}\mathrm{C}}$ %)		W (%)		Mo (%)	
	C_{calc}	C_{exp}	H_{calc}	H_{exp}	Calc	Exp	Calc	Exp	Calc	Exp
$(TPP)_5H_3SiMo_2W_9O_{39}\cdot 6H_2O$	33.5	32.9	2.7	2.8	42.0	37.4	38.4	37.6	4.5	4.4
$(TBP)_6H_2SiMo_2W_9O_{39}$	28.4	28.6	5.4	5.7	38.4	34.5	40.8	42.8	4.7	4.5
$(Ph_6)_5H_3SiMo_2W_9O_{39}\cdot 2H_2O$	43.9	41.9	3.1	3.1	50.7	51.3	32.7	31.1	3.8	3.7
$(Ph_3Et)_5H_3SiMo_2W_9O_{39}\cdot 2H_2O$	30.3	31.3	2.6	2.7	37.4	36.9	41.4	40.1	4.8	4.7
$(Ph_3C_{16})_7HSiMo_2W_9O_{39}\cdot 2H_2O$	48.0	47.2	5.8	6.4	58.0	60.2	27.8	25.9	3.2	3.0
$(TPP)_9H_4Eu(SiMo_2W_9O_{39})_2\cdot 3H_2O$	32.0	31.9	2.4	2.9	38.4	38.9	40.8	39.2	4.7	4.6
$(TBP)_{12}HEu(SiMo_2W_9O_{39})_2\cdot 3H_2O$	27.7	27.7	5.3	5.8	38.1	40.9	39.8	37.9	4.6	4.4
$(Ph_6)_7H_6Eu(SiMo_2W_9O_{39})_2\cdot 4H_2O$	35.5	34.5	2.6	3.1	40.7	41.5	37.7	35.7	4.4	4.2
$(Ph_3Et)_{10}H_3Eu(SiMo_2W_9O_{39})_2\cdot H_2O$	29.7	28.3	2.6	2.8	36.3	41.1	41.0	42.9	4.7	4.6
$(Ph_3C_{16})_{13}Eu(SiMo_2W_9O_{39})_2\cdot 4H_2O$	45.9	45.5	5.5	5.6	55.5	57.3	28.6	28.2	3.3	3.2

draw out satisfactory conclusions confirming the suggested structures. The infrared spectroscopy can be used to fingerprint the heteropolyanion structures in solution and solid, because correlations between spectral peak positions, shapes, and relative intensities suggest identical structures [9]. The IR spectra recorded for RP^+ salts of the studied compounds together with potassium compositions are presented in Fig. 2. These spectra have generally the same bands as the IR spectrum recorded for the potassium compositions (Fig. 2d) and additional bands appear in the region of 500–550 cm^{-1}, 1400–1620 ~3000 cm^{-1} assigned to C–H, C–C oscillations of the aromatic ring (Ph) and other organic derivatives (Ph_3Et, $Ph_3C_{16}H_{33}$) and P–C oscillations.

The luminescence data concerning Eu(III) intensities, lifetimes and quantum yields of the studied RPEuPOM compounds are presented in Table 2.

For europium complexes with the Keggin $SiMo_2W_9O_{39}{}^{8-}$ anion, higher Eu(III) luminescence intensities, in solid and in DMF solution, and higher quantum yields were obtained in the case of the compound with Ph_6 counter cation. The charge-transfer band (320–340 nm), which is present in mixed tungstomolibdate complexes [9–11], plays an important role in emission of these compounds. The use of this band for Eu(III) excitation shows much higher luminescence intensities than that observed in the case of 394 nm excitation, which is easily obtained when exciting with the nitrogen laser. Eu(III) luminescence was quenched after addition of POM to the Eu(III)/DMF solution in the case of TPP and TBP cations. The Ph_6 cation with six phenyl groups can play an antenna effect role [24] in these complexes and as a result more effective luminescence (intensity and quantum yield) is observed. This role is particularly important in diluted solutions. Our experiments show that in the Eu(III) (1×10^{-5} mol/l) and $SiMo_2W_9O_{39}{}^{8-}$ (2×10^{-5} mol/l) solutions the luminescence intensities measured ($\lambda_{max} = 615$ nm) were as follow [11]:

Ph_6 (DMF):Bu_4N^+ (DMF):K^+ (in water) = 37:7:11

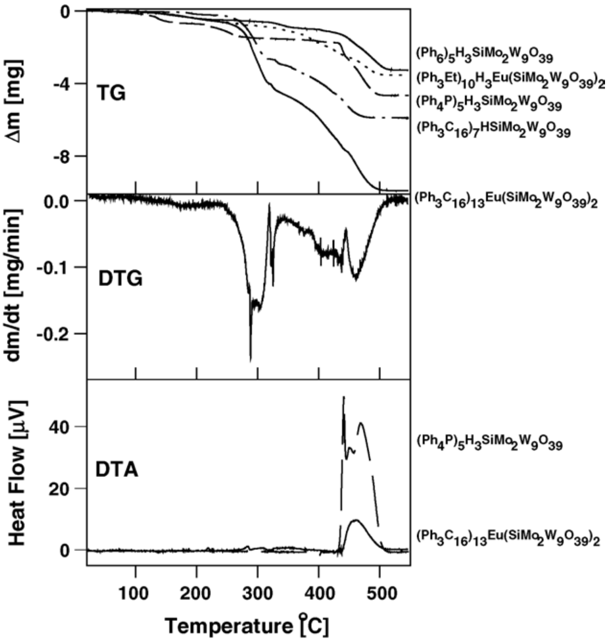

Fig. 1. Thermogravimetric curves (TG, DTG and DTA) for RP-POM and RP-EuPOM.

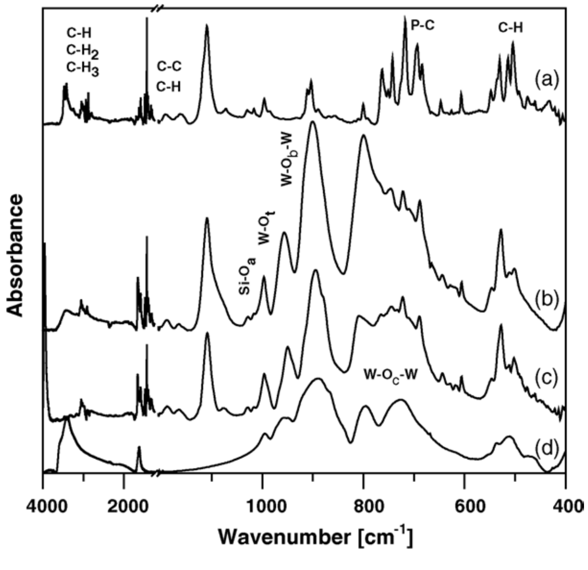

Fig. 2. FTIR spectra of the POM compositions containing organic counter cations: Ph_6 (a), $(Ph_6)_5H_3SiMo_2W_9O_{39}$ (b), $(Ph_6)_7H_6Eu(SiMo_2W_9O_{39})_2$ (c) and $K_8SiMo_2W_9O_{39}$ (d).

Table 2
The luminescence characterization of the RPEuPOM complexes in solid and in DMF

Compound	Lifetime (μs), $\lambda_{exc} = 394$ nm		Luminescence intensity (a.u.)		Quantum yield	
RP-Eu($SiMo_2W_9O_{39}$)$_2$	Solid	Solution $C_{Eu(III)} = 0.001$ mol/l	Solid $\lambda_{max} = 615$ nm	Solution $C_{Eu(III)} = 0.0004$ mol/l	Solid	Solution
Ph_6	484.6	893.8	132.3 (337[a])	198.8 (335[a])	0.0123	0.0035
Ph_3Et	513.4	935.5	94.9 (330)	181.6 (340)	0.0004	0.0024
Ph_3C_{16}	570.1	823.7	91.7 (320)	89.9 (340)	0.0042	0.0011
TPP	517.0	578.8	16.6 (320)	49.0[b](335)	0.0097	–
TBP	511.3	610.3	35.9 (333)	79.0[b](335)	0.0019	–

[a] λ_{exc} (nm).
[b] Eu:POM = 1:1, $C_{Eu} = 0.0005$ mol/l.

The complexation study was tested analyzing absorption spectra of Nd(III) ion in the range of its hypersensitive transition ($^4I_{9/2} \rightarrow {}^2H_{9/2}$). Results indicated formation of the Ln(POM)$_2$ sandwich complexes. Computer-assisted target factor analysis [25] has been applied to the evaluation of the spectra of Nd(III) in DMSO solutions containing varying amounts of the POM. The conditional formation constants for Nd(III) with $\lg \beta_{12} = 8.6 \pm 0.5$, $\lg \beta_{12} = 8.2 \pm 0.4$ and $\lg \beta_{12} = 9.6 \pm 0.7$ were obtained for $(Ph_3Et)_5H_3SiMo_2W_9O_{39}$, $(Ph_3C_{16})_7HSiMo_2W_9O_{39}$ and $(Ph_6)_5H_3SiMo_2W_9O_{39}$, respectively.

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