



## Synthesis and Spectroscopic Studies of Chosen Heteropolytungstates and Their Ln(III) Complexes

STEFAN LIS\* and SŁAWOMIR BUT

Department of Rare Earths, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6,  
60-780 Poznan, Poland

**Abstract.** The heteropolytungstates  $[(\text{Na})\text{P}_5\text{W}_{30}\text{O}_{110}]^{14-}$  (**I**),  $[(\text{Na})\text{Sb}_9\text{W}_{21}\text{O}_{86}]^{18-}$  (**II**) and  $[(\text{Na})\text{As}_4\text{W}_{40}\text{O}_{140}]^{27-}$  (**III**) and the monovacant Keggin structure of the general formula  $[\text{XW}_{11-x}\text{Mo}_x\text{O}_{39}]^{n-}$  (X-Si, P;  $n = 7$  for P and  $8$  for Si) (**IV**) as well as their europium(III) complexes were studied. The structures of **I–IV** as well as the europium(III) encrypted  $[(\text{Eu})\text{P}_5\text{W}_{30}\text{O}_{110}]^{12-}$  (**VI**),  $[(\text{Eu})\text{Sb}_9\text{W}_{21}\text{O}_{86}]^{16-}$  (**VII**),  $[(\text{Eu})\text{As}_4\text{W}_{40}\text{O}_{140}]^{25-}$  (**VIII**) and sandwiched  $[\text{Eu}(\text{XW}_{11-x}\text{Mo}_x\text{O}_{39})_2]^{n-}$  ( $n = 11$  for P and  $n = 13$  for Si) (**V**) complexes were synthesized and spectroscopically characterized. The complexes were studied using UV-Vis absorption and luminescence, as well as the laser-induced europium ion luminescence spectroscopy. Absorption spectra of Nd(III) were used to characterize the complexes formed. Excitation and emission spectra of Eu(III) were obtained for solid complexes and their solutions. The relative luminescence intensities of the Eu(III) ion, expressed as the ratio of the two strongest lines at 594 nm and 615 nm,  $\eta = I_{615}/I_{594}$ , which is sensitive to the environment of the primary coordination sphere about the Eu(III) ion, was calculated. In the case of the sandwiched  $[\text{Eu}(\text{XW}_{11-x}\text{Mo}_x\text{O}_{39})_2]^{n-}$  complexes a linear dependence of the luminescence quantum yield of Eu(III) ion,  $\phi$ , (calculated using  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  as a standard) on the content of Mo (number of atoms,  $x$ ) in the  $[\text{Eu}(\text{XW}_{11-x}\text{Mo}_x\text{O}_{39})_2]^{n-}$  structure was observed.

**Key words:** polyoxometalates, Eu(III) and Nd(III) complexes, absorption and luminescence spectra, quantum yield of Eu(III) luminescence

### 1. Introduction

Among many polyoxometalates anions (POM), there are three of composition  $[(\text{Na})\text{P}_5\text{W}_{30}\text{O}_{110}]^{14-}$  (**I**),  $[(\text{Na})\text{Sb}_9\text{W}_{21}\text{O}_{86}]^{18-}$  (**II**) and  $[(\text{K})\text{As}_4\text{W}_{40}\text{O}_{140}]^{27-}$  (**III**) that function as inorganic cryptands. They can encapsulate selectively alkali metal cations and lanthanide ions [1–5]. Other class of POM complexes can be created from monovacant Keggin anions of the general formula  $[\text{XW}_{11-x}\text{Mo}_x\text{O}_{39}]^{n-}$  (X-Si, P) (**IV**) by forming sandwiched  $[\text{Eu}(\text{XW}_{11-x}\text{Mo}_x\text{O}_{39})_2]^{n-}$  (**V**) complexes [6–8]. The significance and interest of these heteropolyanions relates to their potential antiretroviral activity and wide applications [9, 10]. In this work structures of **I–III** and as well as the europium(III) encrypted  $[(\text{Eu})\text{P}_5\text{W}_{30}\text{O}_{110}]^{12-}$  (**VI**),  $[(\text{Eu})\text{Sb}_9\text{W}_{21}\text{O}_{86}]^{16-}$  (**VII**),  $[(\text{Eu})\text{As}_4\text{W}_{40}\text{O}_{140}]^{25-}$  (**VIII**), and sandwiched (**V**),

\* Author for correspondence.

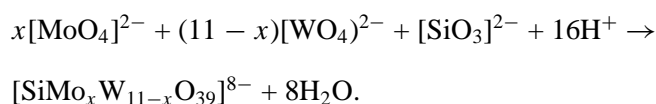
complexes were synthesized and spectroscopically characterized. The compositions of these compounds were verified based on the results from elemental and thermogravimetric analysis, spectroscopic determination of W and Mo contents [11] and infrared spectroscopy.

## 2. Experimental

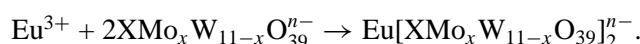
The POMs and their Eu(III) or Nd(III) complexes were prepared according to previously published methods. The inorganic cryptands **I–III** were synthesized and purified as described in earlier procedures [1, 5, 12]. The Eu-encrypted (or Nd) derivatives **VI–VIII** were synthesized from **I–III** according to the literature [2–5].

The Keggin type POM and their Eu(III)-sandwiched complexes were prepared as earlier described in [8, 12].

The general formation process is a condensation of monomeric oxoanions (i.e.,  $\text{WO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{SiO}_4^{2-}$ ,  $\text{AsO}_2^-$  or  $\text{Sb}_2\text{O}_3$ ) in acidic aqueous solution, governed by reaction conditions, notably pH, ratio of reactants, temperature and pressure. The synthesis of Keggin's tungstomolybdic **IV** anions is as follows (according to the synthesis  $[\text{SiW}_{11}\text{O}_{39}]^{8-}$  described in [12]):

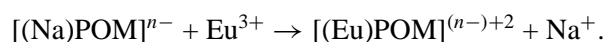


The sandwiched complexes **V** are formed based upon reaction:



To 1 mmol of  $[\text{XMo}_x\text{W}_{11-x}\text{O}_{39}]^{n-}$  dissolved in 10 mL of hot water ( $\sim 90^\circ\text{C}$ ) with small amounts of perchloric acid (to adjust  $\text{pH} \leq 2$ ) was added 0.5 mmol (2.5 mL of 0.2 mol/L)  $\text{Eu}(\text{ClO}_4)_3$  solution. Then potassium acetate was added to adjust the pH of the solution to 4.5–5.0. Next to the hot solution was added 2.5 mL of 4 mol/L KCl solution. The lukewarm mixture was filtered and the filtrate was allowed to stand overnight at low temperature (about  $5^\circ\text{C}$ ). The solid product was washed with cold water and dried at ambient temperature.

The europium encrypted derivatives were prepared by exchanging the alkali metal cation with  $\text{Eu}^{3+}$  (or  $\text{Nd}^{3+}$ ) cation in reaction [1–5]:



Cryptands **VII** and **VIII** react with Eu(III) ion at normal atmospheric pressure whereas the Preyssler anion **VI** requires higher pressure reaction conditions (special reaction vessel) [1–5].

Upon addition of an excess of NaOH the complexes undergo decomposition reactions and after that the contents of tungsten or molybdenum was spectrophotometrically analyzed with tiron [11].

Elemental analysis of the polyoxometalate anions and their europium complexes were taken for a purity check using an Elemental Analyzer 2400 CHN, Perkin Elmer.

Thermogravimetric (TG) analysis were conducted using a Shimadzu TGA-50H/A50 thermoanalytic network system. The conditions of measurements were as follows: temperature interval 25–550 °C, heating rate: 2 °C · min<sup>-1</sup>, specimen weight: ~20 mg, air flux: 100 mL/min, ZnSO<sub>4</sub>·7H<sub>2</sub>O was used as a reference material.

Absorption spectra were recorded on a UV-240H1 PC Shimadzu spectrophotometer and the IR spectra were obtained by means of a FTIR Bruker JFS 113v spectrophotometer, and the samples (1.5 mg) were prepared in KBr (200 mg) or KRS-5 (6 μL, as aqueous solutions).

The corrected luminescence spectra of Eu(III) were recorded using a Perkin-Elmer MPF-3 spectrofluorimeter. The luminescence quantum yield of the Eu(III) ion was calculated using [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> as a standard.

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 relation, providing the decay constants.

### 3. Results and Discussion

Chemical analysis (elemental, thermogravimetric, spectroscopic determination of Mo and W, and IR spectroscopy) lead to the formulae: K<sub>8</sub>SiW<sub>11</sub>O<sub>39</sub> · 17H<sub>2</sub>O, K<sub>8</sub>SiW<sub>11-x</sub>Mo<sub>x</sub>O<sub>39</sub> ~ 17H<sub>2</sub>O, K<sub>13</sub>[Eu(SiW<sub>11</sub>O<sub>39</sub>)<sub>2</sub> · 16H<sub>2</sub>O, K<sub>13</sub>[Eu(SiW<sub>11-x</sub>Mo<sub>x</sub>O<sub>39</sub>)<sub>2</sub>] ~ 28H<sub>2</sub>O, K<sub>12.5</sub>Na<sub>1.5</sub>[(Na)P<sub>5</sub>W<sub>30</sub>O<sub>110</sub>] · 22H<sub>2</sub>O, (NH<sub>4</sub>)<sub>18</sub>[(Na)Sb<sub>9</sub>W<sub>21</sub>O<sub>86</sub>] · 24H<sub>2</sub>O, Na<sub>27</sub>[(Na)As<sub>4</sub>W<sub>40</sub>O<sub>140</sub>] · 71H<sub>2</sub>O, K<sub>12</sub>[(Eu)P<sub>5</sub>W<sub>30</sub>O<sub>110</sub>] · 54H<sub>2</sub>O, (NH<sub>4</sub>)<sub>16</sub>[(Eu)Sb<sub>9</sub>W<sub>21</sub>O<sub>86</sub>] · 40H<sub>2</sub>O and K<sub>25</sub>[(Eu)As<sub>4</sub>W<sub>40</sub>O<sub>140</sub>] · 39H<sub>2</sub>O. Elemental analysis of POMs and their complexes was used only for water determination from the H contents (because no C and N are present), as a supplementary technique for thermogravimetric method. Data obtained from both methods were in good agreement (within 2%).

The results obtained from thermogravimetric analysis indicate that the structures **I**, **II** and **III** are thermostable (up 550 °C, 350 °C and 420 °C, respectively), and their Eu(III) sandwiched complexes (480 °C, 350 °C, 550 °C), whereas the Keggin anions are more thermally stable (550 °C) than their europium sandwiched complexes (380 °C) (Figure 1).

The IR spectra of the structure studied obtained after 5 hour heating at 400 °C and 560 °C are shown in Figure 2, where IR bands in the range of 600–1000 cm<sup>-1</sup> have disappeared.

IR spectroscopy has been used to fingerprint the heteropolyanion structures in H<sub>2</sub>O solutions. A good correlation between spectral peak positions, shapes, and

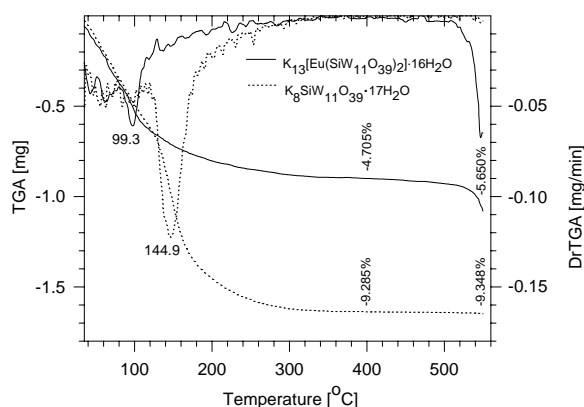


Figure 1. Thermogravimetric results for  $K_8SiW_{11}O_{39} \cdot 17H_2O$  and  $K_{13}[Eu(SiW_{11}O_3)_2] \cdot 16H_2O$  polyoxometalates.

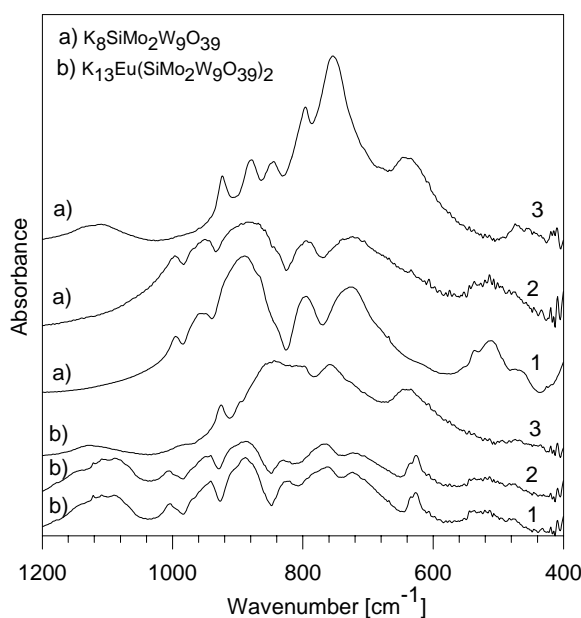


Figure 2. IR spectra of POM studied: 1, recorded at 25 °C; and after 5 h calcination of the powdered samples: 2, at 400 °C and 3, at 560 °C.

relative intensities of the spectra, obtained for solid and solution, strongly indicates identical structures (Figure 3).

The complexes were characterized using Nd(III) absorption of the hypersensitive band at  $\sim 800$  nm. Absorption spectra of Nd(III) of the hypersensitive transition  $^4I_{9/2} \rightarrow ^2H_{9/2}$  were measured for various Nd:POM ratios and at pH  $\sim 5$ . Examples of the spectra for  $Nd(SiW_{11}O_{39})_2^{13-}$  and  $[(Nd)As_4W_{40}O_{140}]^{25-}$  are shown in Figure 4. The spectra relative to that of Nd(III) aqua ion (1) show

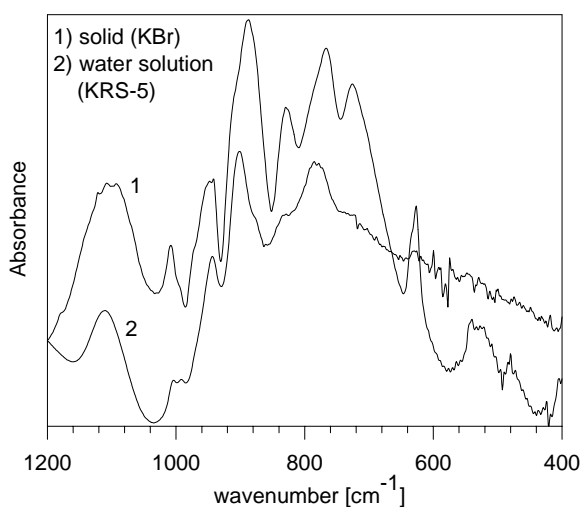


Figure 3. IR spectra of  $K_{13}[Eu(SiW_{11}O_{39})_2 \cdot 16H_2O]$  recorded for solid and saturated water solution.

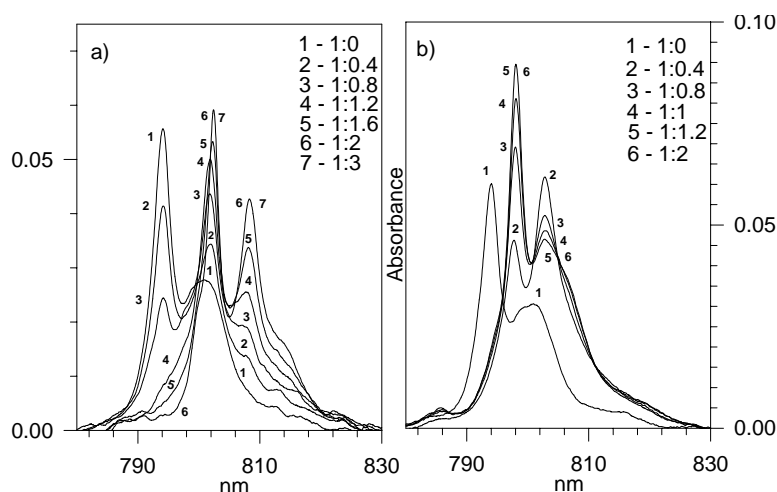


Figure 4. Absorption spectra of Nd(III) in the range of the hypersensitive  $^4I_{9/2} \rightarrow ^2H_{9/2}$  transition: (a) complexes  $Nd(SiW_{11}O_{39})_2^{13-}$  and (b),  $[(Nd)As_4W_{40}O_{140}]^{25-}$ , as function of Nd(III) : POM ratio;  $C_{Nd(III)} = 1 \text{ mmol/L}$ , optical path length 5 cm.

an increase in the intensities as well as a significant shift of the maximum from 794 nm to 803 nm and 808 nm consistent with the  $[(Nd)As_4W_{40}O_{140}]^{25-}$  and  $Nd(SiW_{11}O_{39})_2^{13-}$  complexes, respectively.

The calculated values of the oscillator strengths, shown in Table I, confirm the formation of the 1 : 1 type complexes for **III** and 1 : 1 and 1 : 2 complexes for the Kegin's ligand **IV**.

Table I. Oscillator strength values ( $\times 10^6$ ) calculated for the Nd(III)  $^4I_{9/2} \rightarrow ^2H_{9/2}$  hypersensitive transition

Molar ratio	$\text{SiW}_{11}\text{O}_{39}^{8-}$	$[(\text{Na})\text{As}_4\text{W}_{40}\text{O}_{140}]^{27-}$
1:0	8.3593	8.3593
1:0.4	8.0917	10.7768
1:0.6		11.2195
1:0.8	8.0134	11.8827
<b>1:1</b>		12.1927
1:1.2	8.3237	12.5521
1:1.4		12.4249
1:1.6	9.0367	
<b>1:2</b>	9.2731	12.4632
1:2.4	9.5767	
1:2.8	9.3346	

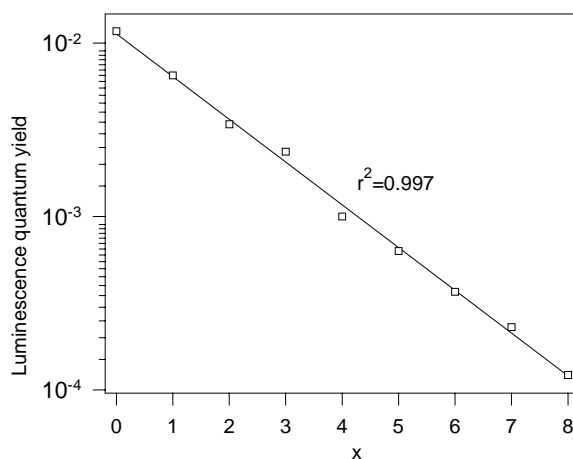


Figure 5. Luminescence quantum yield of  $\text{Eu}^{3+}$  ion as a function of Mo number,  $x$ , in the  $[\text{Eu}(\text{PMo}_x\text{W}_{11-x}\text{O}_{39})_2]^{13-}$  complexes; exc = 394 nm,  $C_{\text{Eu(III)}} = 0.4$  mmol/L, ionic strength = 1 mol/L (KCl).

Excitation and emission spectra of Eu(III) and laser-induced europium ion spectroscopy, obtained for solid complexes and their solutions, were recorded at room temperature. The relative luminescence intensities of the Eu(III) ion, expressed as the ratio of the two strongest lines at 594 nm and 615 nm,  $\eta = I_{615}/I_{594}$ , which is sensitive to the environment of the primary coordination sphere about the Eu(III) ion, were calculated. Calculated  $\eta$  values 1.1 for **VI**, 5.4 and 4.3 for **VII** and **VIII**, and 1.0 ( $x = 0$ ) – 1.6 ( $x = 9$ ) for  $[\text{Eu}(\text{SiW}_{11-x}\text{Mo}_x\text{O}_{39})_2]^{13-}$  **IV**, show the

highest symmetry in the case of  $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$  and  $[\text{Eu}(\text{SiW}_{11-x}\text{Mo}_x\text{O}_{39})_2]^{13-}$  complexes. The  $\eta$  value for the  $\text{Eu}^{3+}$  uncomplexed (nine hydrated) ion is equal 0.3.

Eu(III) luminescence lifetimes, measured both for solid and aqueous ( $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ ) solutions, indicate that the encrypted (VI–VIII) complexes have three or four water of hydration, whereas the sandwiched  $[\text{Eu}(\text{XW}_{11-x}\text{Mo}_x\text{O}_{39})_2]^{13-}$  complexes have no water molecules in the Eu(III) inner coordination sphere. In the case of the sandwiched  $[\text{Eu}(\text{XW}_{11-x}\text{Mo}_x\text{O}_{39})_2]^{13-}$  complexes a linear dependence of the luminescence quantum yield of Eu(III) ion,  $\phi$ , (calculated using  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  as a standard) on the content of Mo (number of atoms,  $x$ ) in the V structure was observed (Figure 5). This dependency can be applied for the determination of the contents of Mo in polytungstomolybdate complexes.

### Acknowledgement

This work was supported by the Polish State Committee for Scientific Research, Grant No. 3 T09A 106 14.

### References

1. I. Creaser, M. C. Heckel, R. J. Neitz, and M. T. Pope: *Inorg. Chem.* **32**, 1573 (1993).
2. M. R. Antonio and L. Soderholm: *Inorg. Chem.* **33**, 5988 (1994).
3. J. Liu, S. Liu, L. Qu, M. T. Pope, and Ch. Rong: *Trans. Met. Chem.* **17**, 311 (1992).
4. J. Liu, J. Guo, B. Zhao, G. Xu, and M. Li: *Trans. Met. Chem.* **18**, 205 (1993).
5. S. Lis, M. Elbanowski, and S. But: *Acta Phys. Pol. (A)* **90**, 361 (1996).
6. M. T. Pope: *Heteropoly and Isopolymetalates*, Springer-Verlag, New York (1983).
7. M. T. Pope and A. Müller: *Angew. Chem. Int. Ed. Engl.* **30**, 34 (1991).
8. R. D. Peacock and T. J. R. Weakley: *J. Chem. Soc. (A)* 1836 (1971).
9. M. T. Pope and A. Müller (eds): *Polyoxometalates: from Platonic Solids to Anti-viral Activity*, Kluwer Academic Publishers, Dordrecht, Boston, London (1994).
10. D. E. Katsoulis: *Chem. Rev.* **98(1)**, 359 (1998).
11. S. Lis and S. But: *Materials Science Forum*, accepted for publication (1999).
12. W. G. Klemperer: Early transition metal polyoxoanions (Chapter 3), *Inorg. Synth.* **27**, 71 (1990).
13. Z. Stryla, S. Lis, and M. Elbanowski: *Optica Applicata* **XXIII**, 163 (1993).

