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SYNTHESIS AND SPECTROSCOPIC STUDY OF EUROPIUM(III) IN HETEROPOLYANION $[EuP_5W_{30}O_{110}]^{12-}$

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The heteropolyanions of Preyssler anion $[NaP_5W_{30}O_{110}]^{14-}$ and its europium-encrypted derivative $[EuP_5W_{30}O_{110}]^{12-}$ were prepared and spectroscopically characterized. The compositions of these heteropolyanions were verified based on the results from elemental and thermogravimetric analysis and the data of spectrophotometric determination of tungsten contents. Absorption in the UV–vis and IR region and luminescence spectra, as well as results of the laser-induced europium ion luminescence spectroscopy, obtained for solid complexes and their solutions, were analysed. Both in solid and solution the europium-encrypted derivative has three water molecules of hydration.

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1. Introduction

The Preyssler heteropolyanion $[NaP_5W_{30}O_{110}]^{14-}$ belongs to few heteropolytungstate anions which encapsulate lanthanide ions [1–3]. The significance and wide interest of lanthanide-encrypted Preyssler anions (and also $[NaSb_9W_{21}O_{86}]^{18-}$ heteropolyanion) concerns their potential antyviral activity and applications in catalysis [2–5]. The $[NaP_5W_{30}O_{110}]^{14-}$ anion consists of five PW_6O_{22} units (derived from the Keggin anion $[PW_{12}O_{40}]^{3-}$) arranged in a crown to form a cylindrical cavity. The Na^+ ion in the Preyssler anion is asymmetrically encapsulated within this cavity and can be replaced by trivalent rare earth ions [2, 6].

In our study the Preyssler heteropolyanion $[NaP_5W_{30}O_{110}]^{14-}$ and its europium-encrypted heteropolyanion $[EuP_5W_{30}O_{110}]^{12-}$ were synthesized according to modified by us previously described methods [1, 2, 4]. We propose a new spectrophotometric procedure of tungsten determination based on previously described for W determination in nuclear materials and steels [7]. Both the parent Preyssler anion and the europium exchanged anion were spectroscopically characterized. Absorption and luminescence spectra, as well as results of the laser-induced europium ion luminescence spectroscopy, obtained for solid complexes and their solutions, are analysed.

2. Experimental

2.1. Synthesis of compounds

2.1.1. Synthesis of the Preyssler heteropolyanion $[NaP_5W_{30}O_{110}]^{14-}$

The Preyssler anion was prepared according to modified by us previously described methods [1,2]. The general formation process is a condensation of monomeric oxoanions (i.e. PO_4^{3-} and WO_4^{2-}) in acidic aqueous solution, governed by reaction conditions, notably pH, ratio of reactants, and temperature. H_3PO_4 (85%, 400 mmol) was added dropwise to $Na_2WO_4 \cdot 2H_2O$ (100 mmol) dissolved in 30 ml of warm water. The mixture containing $[PO_4]$:$[WO_4] = 4:1$ was placed in a sealed sample preparation vessel of 40 ml and heated at 130°C for 20 hours. Upon cooling (to room temperature), an excess of KCl (10 g) was added to precipitate a Preyssler anion (as a fine white powder), which was washed twice in potassium acetate (2 mol/l) and methanol. After two recrystallizations a white needle crystalline of $K_{12.5}Na_{1.5}[NaP_5W_{30}O_{110}]\cdot 15H_2O$ was obtained, with a yield of $\approx$ 20%.

2.1.2. Synthesis of the Eu-encrypted heteropolyanion $[EuP_5W_{30}O_{110}]^{12-}$

Substitution of Na^+ by Eu^{3+} demonstrates the reaction below [2,3]:

$$[NaP_5W_{30}O_{110}]^{14-} + Eu^{3+} \rightarrow [EuP_5W_{30}O_{110}]^{12-} + Na^+$$

$K_{12.5}Na_{1.5}[NaP_5W_{30}O_{110}]\cdot 15H_2O$ (1 g) was dissolved in water (12 ml) and solution was heated to $\approx$ 70°C. One equivalent of $EuCl_3$ was dropwise added to this solution and pH was kept $\approx$ 5.5. The replacing reaction was carried out in a sealed sample preparation vessel and heated at 170°C for 45 hours. After the solution was cooled, the product was precipitated by the addition of KCl (4 g), then filtered and washed twice with ice cold water, and air-dried. After purification a yield of $\approx$ 90% was obtained for $K_{12}[EuP_5W_{30}O_{110}]\cdot 54H_2O$ (a white powder) europium exchanged heteropolyanion. For the studies in D_2O, samples of the Preyssler anion, after dissolving in D_2O, were evaporated to dryness, followed by dissolution in D_2O (repeated 4 times).

2.2. Methods

Elemental analysis of the parent Preyssler anion and the europium exchanged anion were used for a purity checking on an Elemental Analyser 2400 CHN, Perkin Elmer. Termogravimetric (TG) and differential thermal (DTA) analysis were conducted using a Shimadzu TGA-50H/A50 thermoanalytic network system. The conditions of measurements were as follows: temperature interval 273–1173 K, heating rate: 3 K min^{-1}, specimen weight: $\approx$ 20 mg, nitrogen or air flux: 100 ml/min; $ZnSO_4 \cdot 7H_2O$ was used as a reference material.

The spectrophotometric determination of tungsten was made by extraction with 8-hydroxyquinoline from chloroform. We propose a new procedure of tungsten determination, based on previously described for W determination in nuclear materials and steels [7].

The Eu(III) corrected luminescence spectra were registered using Perkin–Elmer MPF-3 spectrofluorimeter and the exciting wavelength was 394 nm. 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 [8]. The luminescence decay curves observed in this work were analysed by a single exponential relation, providing the decay constants. The IR spectra were obtained by means of FTIR Bruker JFS 113v spectrophotometer, and the samples (1.5 mg) were prepared in KBr (200 mg).

3. Results and discussion

The results obtained by thermogravimetric and elemental analysis indicate a content of 15 water molecules per one molecule of the Preyssler anion and 54 water molecules per its molecule of europium-encrypted derivative. Content of tungsten in heteroanions studied was determined spectrophotometrically. The procedure is based on a preliminary extraction with oxine-chloroform from hydrofluoric acid solution in order to remove impurities interfering in W determination. After addition of boric acid and adjustment of the pH to 2.0, W is extracted. An excess of oxine and interfering metal oxine complexes were washed from the chloroform phase with ammonium sulphate–sulfuric acid solution. Chloroform extract after filtering was used for tungsten spectrophotometric determination. For samples containing tungsten absorption at 358 nm was measured (Fig. 1) in 1 cm cells, against chloroform as a reference. The dependence of tungsten absorbance on its concentration is linear in the range from 100 to 700 mg W/20 ml. The plot of a calibration curve for W absorbance versus its concentration is shown in Fig. 2. The results of tungsten contents obtained from spectrophotometric determination, presented in Table I, indicate 65.8% of W in the Preyssler salt and 60.1% of W in its europium derivative and these values correspond to 30 W atoms per molecule of heteropolyanion studied.

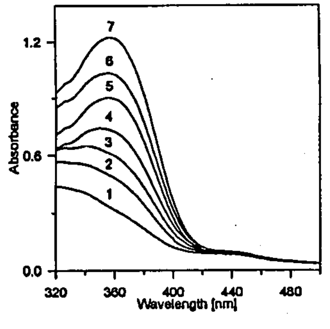


Fig. 1. Absorption spectra of tungsten 8-hydroxychinolinate as a function of W concentration. Concentration of W was: 1 — 5, 2 — 10, 3 — 15, 4 — 20, 5 — 25, 6 — 30, and 7 — 35 μg ml^{-1}.

Both the parent Preyssler anion and the europium exchanged anion were spectroscopically characterized. The IR spectra of both the parent Preyssler anion and its Eu(III)-exchanged form are shown in Fig. 3, and are similar to previously obtained [2,6,9]. The FTIR spectra recorded consist of four regions which correspond to metal–oxygen oscillations [10,11]: 900–600 cm^{-1} (W–O–W, bending), 1000–900 cm^{-1} (W–O, stretching), 1200–1000 cm^{-1} (P–O, ionic stretching),

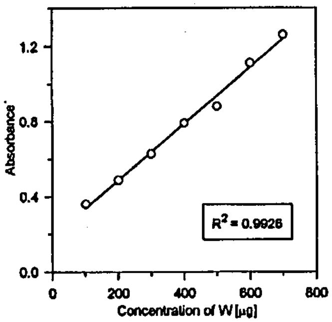


Fig. 2. Plot of a calibration curve for absorbance of tungsten 8-hydroxychinolate versus tungsten concentration (µg W/100 ml) in spectrophotometric determination of tungsten contents.

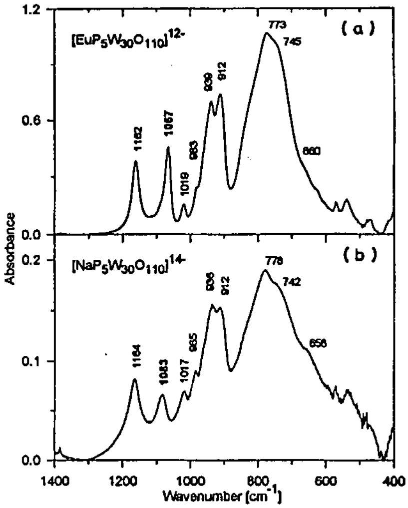


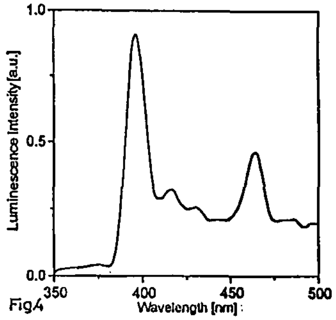
Fig. 3. IR spectra of the Preyssler anion (a) and its europium-encrypted derivative (b).

and O–H oscillation region with two maxima at ≈ 3650 cm^{-1} (stretching) and 1610 cm^{-1} (bending). The last mentioned O–H region indicates crystalline water [11]. Analysis of the FTIR spectra makes possible to observe an effect of a rigidity of the systems studied. On the basis of the FTIR spectra a strengths of vibrations of these parts of the Preyssler anion, which are involved in Eu(III) encapsulation, are analysed. The observed shifts of characteristic bands corresponding to such vibrations proved a weakening of the vibration bands involving the P–O stretching band at $\lambda_{max} = 1083$ cm^{-1} for Preyssler exchanged and at $\lambda_{max} = 1067$ cm^{-1} for the parent Preyssler anion.

Excitation and emission luminescence spectra of $[EuP_5W_{30}O_{110}]^{12-}$ are shown in Figs. 4 and 5. The Eu(III) emission spectrum shows two most intense bands at 592 and 615 nm, associated with $^5D_0 \to {}^7F_1$ and $^5D_0 \to {}^7F_2$ (exhibiting

TABLE I
Contents of tungsten determined in the Preyssler anion and its europium-encrypted derivative.

Composition	W contents [mass percent]		Number of W atoms
	found	calculated	
$K_{12.5}Na_{1.5}[NaP_5W_{30}O_{110}]\cdot 15H_2O$	65.8 ± 1.3	66.9	29.5 ± 0.6
$K_{12}[EuP_5W_{30}O_{110}]\cdot 54H_2O$	60.1 ± 0.8	61.1	29.5 ± 0.4



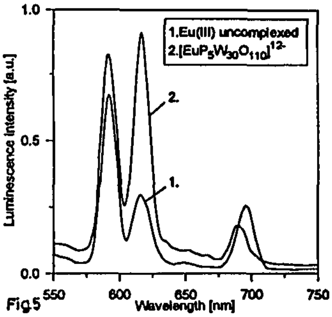


Fig. 4. Luminescence excitation spectrum of $[EuP_5W_{30}O_{110}]^{12-}$ anion, $\lambda_{em} = 615$ nm.
Fig. 5 Luminescence emission spectra of Eu(III) aquo-ion and the europium-encrypted Preyssler anion, $\lambda_{ex} = 394$ nm.

hypersensivity) transitions. Figure 5 presents the spectrum of Eu(III) uncomplexed (aquo-) ion and of the europium-encrypted Preyssler anion. The relative intensities (ratio of I_{615}/I_{592}) are sensitive to the primary coordination sphere of the Eu(III) ion. The luminescence intensity of Eu(III) aquo-ion at 615 nm is weaker than that at 592 nm ($I_{615}/I_{592} = 0.3$) and in the case of europium-encrypted Preyssler luminescence intensity at 615 nm is more intense than that at 592 nm ($I_{615}/I_{592} = 1.1$) indicating complexation (encapsulation) of the Eu(III) ion.

The Eu(III) luminescence lifetimes measured for the solid composition of $K_{12}[EuP_5W_{30}O_{110}]\cdot 54H_2O$ (or $K_{12}[EuP_5W_{30}O_{110}]\cdot 54D_2O$) and its solution ($H_2O$ and D_2O), as shown in Table II, were used to calculate the number of water molecules bond in the inner sphere of the Eu(III) ion from the equation below [12]:

$$n_{H_2O} = 1.05(\tau_{H_2O}^{-1} - \tau_{D_2O}^{-1}). \qquad (1)$$

The calculated hydration number in both cases (solid and solution) is three and indicates a replacement of six water molecules in the Eu(III) inner sphere when encapsulated in the Preyssler anion (Table II).

It is difficult to explain the presence of three water molecules in the cylindrical cavity of the heteropolyanion since its diameter is too small (4 Å) to fit the Eu(III) ion with coordinated water molecules [4]. It is most likely that the Eu(III) ion is not symmetrically encrypted but near to the end of the anion cylinder, and so that some of the water is not directly encrypted. This is in agreement with other authors which postulated the occurrence of two different Eu(III) sites: in

TABLE II

Luminescence lifetime of Eu(III) ion measured for europium-encrypted Preyssler anion in solid and solution (H_2O and D_2O) and calculated hydration number.

System	τ [ms]		n_{H_2O}
	H_2O	D_2O	
Solution of $[EuP_5W_{30}O_{110}]^{12-}$	0.2959	0.3171	3.1
Solid $K_{12}[EuP_5W_{30}O_{110}]\cdot 54H_2O$	2.5205		3.1
or $K_{12}[EuP_5W_{30}O_{110}]\cdot 54D_2O$		5.0292	3.1

site A there are three water molecules coordinated to Eu(III), whereas there are only two water molecules coordinated at site B [4]. Our samples were synthesized with 1 equivalent of Eu(III) and only site A was observable in all the measured samples.

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