

## SYNTHESIS AND SPECTRAL CHARACTERIZATION OF A NEW LANTHANIDE SANDWICH-TYPE TRILACUNARY KEGGIN POLYOXOMETALATE

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### Abstract

Lanthanide polyoxometalates (POM) can be used in conventional syntheses to build up two dimensional materials. Linking up of lacunary POM subunits is accomplished by binding of lanthanides to terminal oxygen atoms of an adjacent polyoxometalate results to synthesis of dimers. The appropriate cations can link the dimers into a lattice, as found in the case of  $\text{Ln}^{3+}$ . Discovery of novel polyoxometalate structures from unexpected route can be guidance for understanding the formation mechanism of polyoxometalates. In our publication, a novel polyoxometalate connected via trivalent lanthanide cation-bridge was designed and synthesized on the basis of the abduction of  $\text{Al}^{3+}$  in aqueous solution. Samarium (III) was chosen as the specific lanthanide. Reaction of the trilacunary  $[\text{PW}_9\text{O}_{34}]^{9-}$  ligand with Sm (III) produces a new sandwich-type polyoxometalate of the type  $[\{\text{Ln}_3\text{O}_3(\text{H}_2\text{O})_2\}(\text{PW}_9\text{O}_{34})_2]^{15-}$  which was synthesized and studied using spectroscopy. The stoichiometry of the trilacunary Keggin 9-tungstophosphate reaction with Sm (III) ions was determined with the aid of conductometric titration of aqueous solution. The aforesaid complex was isolated as a sodium salt and characterized by means of elemental analysis, infra red and electronic spectra.

**Keywords:** Trilacunary POM, trivalent lanthanide cation, sandwich complex, spectral characterization



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### 1. Introduction

Diverse magnetic and electronic properties of 4f lanthanide (Ln) ions have rendered the Ln-containing polyoxotungstates (POTs) a prime target in new polyoxometalates (POMs) material synthesis over the last two decades. [1-6]. The different coordination geometries of the lanthanide cations and the vacant sites afforded by the polyoxometalates usually result in large polyoxometalate clusters [7], showing very interesting electroluminescence and photoluminescence activity [8, 9] as well as enhanced efficiency against HIV [10]. Incorporation of rare earth metal ions in the lacunary polyoxometalate fragments can also lead to lanthano-POMs with remarkable structural features along with interesting magnetic properties. [11, 12]

The first complex of monolacunary Keggin anion  $[PW_{11}O_{39}]^{7-}$  with lanthanides was prepared by Peacock and Weakley [13] in 1971. Sadakane et al [14] reported 1:1 $[Ln(\alpha-SiW_{11}O_{39})(H_2O)_3]^{5-}$  ( $Ln = La(III), Ce(III)$ ) compounds in which the lanthanide cations are octa-coordinated. Some recent publications cited couple of nano-sized lanthano-POM like  $[Pr_6Mo_{120}]$  [15],  $[Eu_4Mo_{128}]$  [16] or  $[Ce_{16}W_{148}]$  [17] which can be formed through the coordination of Ln (III) ions by the outer oxygen atoms of POM anions. However, the first trilacunary Keggin complex with lanthanide ions was reported by Knoth in 1986 [18]. In this research article, the synthesis and characterization of a new Samarium incorporated lanthanide complex  $[Ln_3O_3(H_2O)_2](PW_9O_{34})_2]^{15-}$  [where  $Ln(III) = Sm$ ] is reported. This complex has a sandwich-type structure consisting of two  $[PW_9O_{34}]^{9-}$  (PW9) units connected by a belt of three lanthanides, alternating with the three terminal oxygen atoms. This research result suggests a sandwich-type structure similar to the structure of the Ce(IV) complex reported by Knoth et al. This work demonstrates a simple synthetic strategy of using lacunary POT precursors to assemble with in-situ generated Sm–O clusters in certain pH, which exert a slow-releasing effect for  $Sm^{3+}$  ions in acidic conditions. Many factors can affect the isolation of final products, such as initial reactants, the concentrations of counter cations, pH values, reaction time and temperature. In our case, the pH value of the reaction system was of crucial importance for the product formation.

## 2. Experimental

### 2.1. Materials and methods

Reagent grade chemicals were used and all syntheses and studies were carried out in distilled water. Chemicals were readily available from commercial sources (Merck, India) and were used as received without further purification.

### 2.2 Preparation of complexes

#### 2.2.1. Preparation of the precursor ligand $Na_9[PW_9O_{34}]$ (1)

$Na_2WO_4 \cdot 2H_2O$  is dissolved in 30ml of water and then 85%  $H_3PO_4$  is added drop wise with stirring (0.8ml) to achieve pH at 8. Later on glacial AcOH is added drop wise with vigorous stirring to achieve the final pH of 7.5. During addition of AcOH, large quantities of white precipitate are formed. The solution is then stirred for 1hr and the precipitate is collected & dried by suction filtration. The same synthetic procedure was followed as reported by Knoth et al [19].

#### 2.2.2. Preparation of $Na_{12}H_3[Sm_3O_3(H_2O)_2](PW_9O_{34})_2 \cdot 18H_2O$ (2)

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1.6 mmol (0.58 g) sample of  $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$  was dissolved in 20 mL of distilled water, and added drop wise, while stirring, to an aqueous solution (50 ml) of  $\text{Na}_9[\text{PW}_9\text{O}_{34}]$  (5 g, 2.04 mmol). The slightly turbid final solution was refluxed for 1 h, its pH adjusted to 5 with 6M HCl and then filtered under suction. The filtrate was heated at  $80^\circ\text{C}$ , while stirring, until reduced to half of its volume. It was then cooled to room temperature. A few days later a yellowish white precipitate appeared. The crude product was filtered off and recrystallized in the luke warm water. Pale yellow-green crystalline powder was obtained by cooling in  $5^\circ\text{C}$ . Elemental analysis: calculated for  $\text{Na}_{12} \text{H}_{43} \text{Sm}_3 \text{O}_{91} \text{P}_2\text{W}_{18}$  : H, 1.21; N, 4.19; found: Sm 5.99; Na 22.74; P 0.88; W 47.19%. Found: Sm 5.89; Na 22.81; P 0.81; W 47.31%.

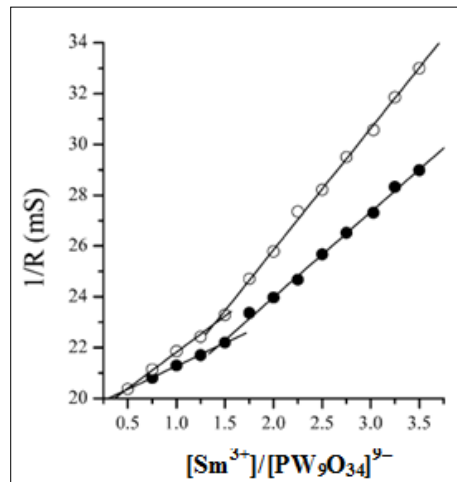
### 2.3 Physical measurements

Elemental analyses were carried out using a Perkin–Elmer 240 elemental analyzer. UV-Vis spectra were recorded on a Perkin-Elmer Lambda 19 spectrometer using Teflon-stoppered quartz cells with a path length of 1 cm. IR spectra ( $400\text{--}4000 \text{ cm}^{-1}$ ) were recorded in KBr pellets on a Nicolet Magna IR 750 series-II FTIR spectrophotometer. Electrochemical experiments were performed using a potentiostat with data acquisition (Autolab, ECO Chemie, Utrecht, Netherlands). A conventional three electrode cell was used, using a graphite disk ( $F = 5 \text{ mm}$ ) as a working electrode, a saturated calomel electrode (SCE) as a reference electrode and a Pt foil as a counter electrode. All measurements were performed at room temperature in phosphate ( $\text{NaHPO}_4\text{--H}_3\text{PO}_4$ ) buffer solutions (pH 3-5.5). The pH measurements were carried out using a digital pH-meter (citronic) equipped with a combined glass electrode (Metrohm, Switzerland). For each measurement a  $6 \times 10^{-3} \text{ M Sm}^{\text{III}}\text{PW}_9$  solution (2 ml) was dissolved in the buffer solution (10 ml).

### 3. Results and discussion

The trilaconary  $[\text{PW}_9\text{O}_{34}]^{9-}$  anion reacts with  $\text{Sm}(\text{III})$  solution to produce the sandwich-type polyoxometalate  $[\{\text{Sm}_3\text{O}_3(\text{H}_2\text{O})_2\}(\text{PW}_9\text{O}_{34})_2]^{15-}$  (2) in modest yield. Conductometric titration of  $\text{PW}_9$  solution with  $\text{Sm}^{3+}$  ions were performed to establish the complexes composition in solution,. The titration results showed a breakpoint at 3:2  $\text{Ln}^{\text{III}} : \text{PW}_9$  ratio (Fig.1). The pH range, in which the  $\text{Sm}^{\text{III}}\text{PW}_9$  complex was formed was determined by spectrophotometry ( $\lambda = 280 \text{ nm}$ ) of some  $\text{Sm}^{\text{III}} : \text{PW}_9 = 3:2$  stoichiometric mixtures at various pH ranges. It resulted that this

compound is stable in the pH range of 3–7, also displaying a maximum absorbance level at the pH value of 5.

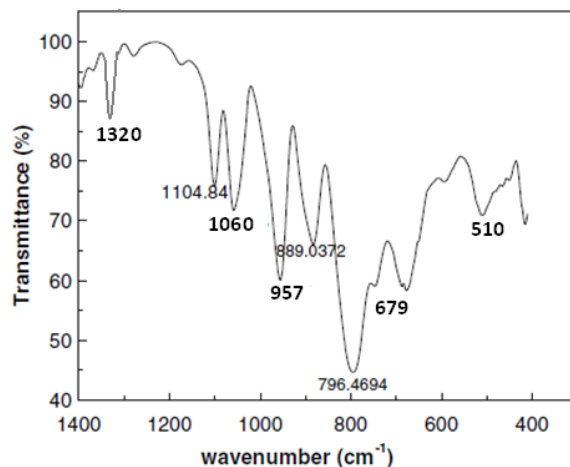


**Fig.1. Conductometric titrations of trilacunary PW<sub>9</sub> anion with Sm<sup>3+</sup> ion**

### 3.1 Vibrational Spectroscopy

The IR spectra of **(1)** display the characteristic features of a typical trilacunary Keggin-type structure. That is why PW<sub>9</sub> shows usual five strong symmetric and asymmetric stretching frequencies at 945 cm<sup>-1</sup> [ $\nu_{as}(W=O_t$  with terminal oxygen O<sub>t</sub>)], shoulder peak at 880cm<sup>-1</sup> [ $\nu_{as}(P-O_i$  with internal oxygen atom which links P and W)], 795cm<sup>-1</sup> [ $\nu_s(W-O_e-W$  where O<sub>e</sub> connects edge-sharing octahedra,)], 770cm<sup>-1</sup> [ $\nu_s(W-O_c-W$  octahedral corner sharing )] and 510cm<sup>-1</sup> [ $\nu_s(W-O_{c,e}-W$  where O<sub>c,e</sub> connects corner and edge-sharing octahedra,)]. Similarity of FT-IR spectra for PW<sub>9</sub> **(1)** and for Sm<sup>III</sup>PW<sub>9</sub> **(2)** shows that vibration bands are mainly due to the polyoxotungstates (POT) structure. When comparing the IR spectra of Sm<sup>(III)</sup>PW<sub>9</sub> **(2)** complex with that of the PW<sub>9</sub> ligand **(1)**, a shift of the antisymmetric stretching vibrations  $\nu_{as}(P-O_i)$ , the main band of the ligand, appearing in the 1200-700 cm<sup>-1</sup> range towards higher frequencies indicates that the coordination of the lanthanide ions increases the cohesion of the trilacunary structure.(Fig.2) [20]. The tiny shift of the  $\nu_{as}(W=O_t)$  stretching vibration in the spectra of Sm<sup>III</sup>PW<sub>9</sub> complex as compared to PW<sub>9</sub>, can be explained by the fact that terminal O<sub>t</sub> atoms are not involved in the coordination of lanthanide Sm(III) ion. On the other hand, the larger shift of the  $\nu(W-O_{c,e}-W)$  stretching vibrations for the bonds from the belt and cap areas indicates the coordination of Sm(III) ions by O<sub>c</sub> and O<sub>e</sub> oxygen atoms from corner-sharing and edge-sharing

octahedra. This results to a new symmetric stretching frequency band for (Sm–O–W) at 1320  $\text{cm}^{-1}$ . Apart from these, in the range 1000-700  $\text{cm}^{-1}$ , the complex exhibits a new band, due to the asymmetric stretching vibrations of the bridges  $\nu_s(\text{W-O}_b\text{-W})$ , proving the presence of two  $\text{PW}_9\text{O}_{34}$  units connected by bridging  $\text{O}_b$  atoms. The other new  $\nu(\text{Sm-O}_{c,e})$  bands, expected in the 500-300  $\text{cm}^{-1}$  range, are masked by the stronger vibration band of the ligand in this area. Five strong vibration bands are indeed observed for  $\nu(\text{P-O})$ ,  $\nu(\text{W=O})$ , and  $\nu(\text{W-O-W})$  at 1104.8, 1060, 957, 889, and 796.5  $\text{cm}^{-1}$ . That shows a splitting of the P–O stretching band (1104.8 and 1058.7  $\text{cm}^{-1}$ ), indicative of the lacunary anion and originating from the loss of an {W–O} unit from  $[\text{PW}_{12}\text{O}_{40}]^{3-}$ , which is identical with that of  $[\text{Ln}(\text{PMo}_{11}\text{O}_{39})_2]^{11-}$  [21]. The splitting of the characteristic P–O asymmetric stretching vibration between 1100 and 1000  $\text{cm}^{-1}$  suggests a decrease in the  $\text{PO}_4$  group symmetry by coordination of the lanthanide ions to the ligand [22]. The lack of the P=O band above 1100  $\text{cm}^{-1}$  in the infrared spectra of the  $\text{PW}_9$  ligand and  $\text{Sm}^{\text{III}}\text{PW}_9$  polyoxometalate complexes proves that both of them have A-type structures and therefore the preservation of the A- $\text{PW}_9$  fragments in the  $\text{Sm}^{\text{III}}\text{PW}_9$  complex is confirmed [23]. The red shifts of  $\nu(\text{W=O})$  and  $\nu(\text{W-O-W})$  can be ascribed to the influence of incorporating Sm ions into the polyanion framework. In addition, a strong broad peak observed at 3350  $\text{cm}^{-1}$  is assigned to  $\nu(-\text{OH})$  absorption along with the hydrogen bonds which proves the presence of lattice water.



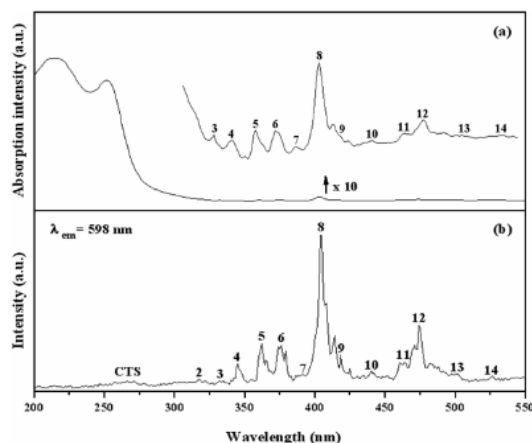
**Fig-2: FTIR spectrum of complex 2, taken as KBr pellet**

### 3.2 Electronic spectroscopy

The UV-electronic spectra of the  $PW_9$  ligand and  $Sm^{III}PW_9$  complexes (Fig.5) exhibit two characteristic bands at  $\sim 200$  and  $\sim 250$  nm, assigned to  $W-O_t$  and  $W-O_b-W$  transitions respectively. ( $O_t$  is a terminal oxygen and  $O_b$  is a bridging oxygen) [24]. In both polyoxometalate complexes these bands are shifted to lower frequencies by comparing with the  $PW_9$  ligand, due to the coordination of the lanthanide cations. The  $Sm^{III}PW_9$  complex exhibits an additional metal-to ligand charge transfer band at  $\sim 280$  nm of the  $Sm^{3+}-O^{2-}$  ions [25]. UV spectra of the  $PW_9$  ligand and  $Sm^{III}PW_9$  complex are also very similar, evincing that the charge transfer inside the polyoxotungstate structure is not significantly affected by coordination. However, the molar absorption coefficient  $\epsilon$  of the  $\nu_2$  band, which is proportional to the number of W atoms, is almost twice greater in complexes than in the  $PW_9$  ligand ( $\epsilon \approx 1.40 \times 10^5$  vs.  $0.75 \times 10^5$   $L\ mol^{-1}\ cm^{-1}$ ). These values also indicate the existence of two  $PW_9O_{34}$  trilacunary units.

### 3.2.1 Excitation and emission spectra of $Sm^{3+}$ ion in $Sm^{III}PW_9$ complex solution

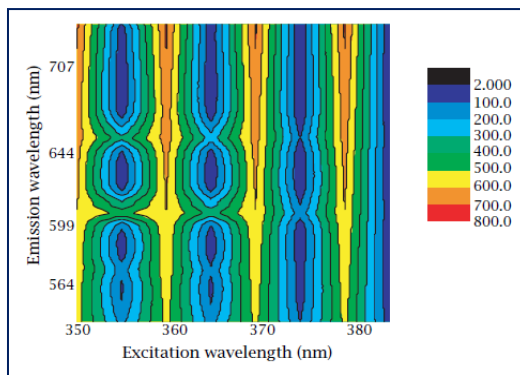
Fig.3(b) shows an excitation spectrum of  $Sm^{3+}$  ion in aqueous solution of  $Sm^{III}PW_9$  complex. The excitation spectrum is monitored at 600 nm. A series of excitation peaks in the range from 292 to 490 nm are due to the typical intra-4f ( $4f^3 \rightarrow 4f^3$ ) transitions of the  $Sm^{3+}$  ions that appear at 345, 361, 376, 391, 404, 418, 440, 464 and 474 nm, which were attributed to ( ${}^6H_{5/2} \rightarrow {}^3H_{7/2}$ ), ( ${}^6H_{5/2} \rightarrow {}^4F_{9/2}$ ), ( ${}^6H_{5/2} \rightarrow {}^4D_{5/2}$ ), ( ${}^6H_{5/2} \rightarrow {}^6P_{7/2}$ ), ( ${}^6H_{5/2} \rightarrow {}^4K_{11/2}$ ), ( ${}^6H_{5/2} \rightarrow {}^6P_{5/2} + {}^4M_{19/2}$ ), ( ${}^6H_{5/2} \rightarrow {}^4G_{9/2} + {}^4I_{15/2}$ ), ( ${}^6H_{5/2} \rightarrow {}^4F_{5/2} + {}^4I_{13/2}$ ). From the figure, an intense excitation band was observed at 401 nm. Hence, the emission spectra were recorded with 401 nm excitation which is the most prominent excitation band. After investigation of different optical transitions of  $Sm^{3+}$  ion, it has been found that the main absorption band lies at 401 nm ( $Sm^{3+}: {}^6H_{5/2} \rightarrow {}^6P_{3/2}$ ) which is the characteristic peak for  $Sm^{3+}$  ion. The emission spectra consist of four principal bands associated with  $4f^3 \rightarrow 4f^3$  transitions from  ${}^4G_{5/2}$  level to  ${}^6H_{5/2}$  (563 nm),  ${}^6H_{7/2}$  (601nm),  ${}^6H_{9/2}$  (648 nm) and  ${}^6H_{11/2}$  (710 nm) levels. The most intense emission is observed for  ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$  transition, which leads to a bright orange-reddish emission.



**Fig. 3 (a) Absorption and (b) excitation spectra ( $\lambda_{em} = 598$  nm) for  $\text{Sm}^{\text{III}}\text{PW}_9$  complex**

The excitation bands for  $\text{Sm}(\text{III})$  anionic complex under the orange emission of 596 nm show four main peaks, 222.5 nm, 242 nm, 259 nm and 271 nm. Contour view of the emission spectra of  $\text{Sm}^{3+}$  ion in  $\text{Sm}^{\text{III}}\text{PW}_9$  complex is given below in  $\text{H}_2\text{O}$  at different excitation wavelengths in fig.4. Moreover, lanthanide ions do not contribute to the spectra of their complexes since f-f transitions are Laporte-forbidden and very weak (molar absorptivity coefficients of the order of only  $0.5\text{--}3.0\text{M}^{-1}\text{ cm}^{-1}$ ) [26]. On the other hand, charge-transfer bands involving lanthanide orbitals are also typically not observed in the near-UV and spectral regions [27]. Hence the absorption bands of samarium complexes in different solvents as well as in viscous or polymeric media are completely attributable to the ligand-centered (LC) transitions, although with respect to the corresponding free ligand, some perturbation is observable upon complexation [28]. Lanthanide ion absorption (in the UV-visible and the near IR region) and luminescence are characterized by narrow bands which are ascribed to internal transitions within the 4f shell (i.e. f – f transitions) and, since  $\Delta l = 0$ , are Laporte forbidden. However, 4f electrons are buried within the inner electron core and symmetry distortion upon bonding is minimal. Therefore, f  $\rightarrow$  f transitions are weaker and sharper than d  $\rightarrow$  d transitions and the ligand field effect is considerably smaller. Hypersensitive transitions (the f – f transitions in which the absorption maximum and intensity are sensitive to the ligand field) were used to evaluate the site symmetry and nephelauxetic effect of the lanthanide-polyoxometalate sandwich complexes,  $\text{Ln}(\text{POM})_2$  [29]. In each ligand, the oxygens of the binding site approximately define a square. In the sandwich complex, the two square binding sites are superimposed to give either an eclipsed

(point group  $D_{4h}$ ) or an staggered (point group  $D_{4d}$ ) arrangement. Evaluation of the splitting of  ${}^7F_0 \rightarrow {}^5D_2$  and  ${}^7F_0 \rightarrow {}^5D_1$  excitation bands in Ln-POM complexes indicates their low symmetry. Unsaturated trilacunary polyanions  $[PW_9O_{34}]^{9-}$  exhibit a ligand field strength distinctly weaker than  $H_2O$  [30]. Furthermore, due to the weak nature of f—f transitions, the sensitivity of absorption measurements are limited.



**Fig -4. Contour view of the emission spectra of  $Sm^{3+}$  ion in  $Sm^{III}PW_9$  complex in  $H_2O$  at different excitation wavelengths**

#### 4. Conclusion

A new lanthano heteropolyoxometalate complex  $[\{Sm_3O_3(H_2O)_2\}(PW_9O_{34})_2]^{15-}$  was synthesized by the reaction of Sm(III) ions with the trilacunary Keggin 9- tungstophosphate, after establishing the reaction stoichiometry. All the spectroscopic studies suggest that it has a sandwich-type structure which is a novel feature for samarium(III) ion. In this research paper, the structural features have been established and elucidated with the help of spectroscopy which is a new approach. The gigantic structures like POM can also be investigated prior crystal structure determination by this spectral method which could be a new pathway for crystal structure analysis.

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