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Synthesis and characterisation of two new lanthanide sandwich-type heteropolyoxometalates

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Abstract

The sodium and cesium salts of two new heteropolyoxometalate complexes $[\{Ln_3O_3(OH_2)_2\}(PW_9O_{34})_2]^{15-}$ were synthesized and studied using spectroscopy and cyclic voltammetry. The stoichiometry of the trilacunary Keggin 9-tungstophosphate reaction with Ln(III) ions was determined with the aid of conductometric titrations of aqueous solutions. Ion-exchange as well as ES-MS experiments provided evidence for covalent, inner-sphere bonding of lanthanide cations to the trilacunary α-$[PW_9O_{34}]^{9-}$ heteropolyanion. Cyclic voltammograms of $[\{Ln_3O_3(OH_2)_2\}(PW_9O_{34})_2]^{15-}$ exhibited two pairs of reduction/oxidation waves with negative half-wave potential ($E_{1/2}$) values. These waves were attributed to redox processes corresponding to the polyoxotungstate framework. The redox processes of the Ce derivative revealed the presence of two types of cerium ions.

Keywords: Heteropolyoxometalates; Redox process; Spectroscopy

1. Introduction

Polyoxometalate derivatives of lanthanides are currently under extensive investigation for both fundamental and practical points of view, due to their unique structural, chemical and electronic properties [1]. The different coordination geometries of the lanthanide cations and the vacant sites afforded by the polyoxometalates usually result in large oxometalate clusters [2–10], showing very interesting electroluminescence and photoluminescence activity [1,11–17] as well as enhanced efficiency against HIV [18,19].

The first complexes of monolacunary Keggin and Dawson anions ($SiW_{11}O_{39}^{8-}$, $PW_{11}O_{39}^{7-}$ and $P_2W_{17}O_{61}^{10-}$) with lanthanides were prepared by Peacock and Weakley [20,21] in 1971. Spectrophotometric titration of lanthanides with unsaturated polyoxometalate ligands shows that in solution a well definite 1:1 complex is formed before the 1:2 complex. In these complexes, lanthanide cations are coordinated to four oxygen atoms of each of two monovacant anions in square antiprismatic coordination.

Bartis [22] has shown that in $[Ln(XW_{11}O_{39})(H_2O)_x]^{y-}$ complexes the most common coordination numbers are 8, 9 or 10 because coordinated aqua molecules are present and raise the true coordination number.

Sadakane [23] reported 1:1 $[Ln(\alpha\text{-}SiW_{11}O_{39})(H_2O)_3]^{5-}$ ($Ln = La^{III}$, Ce^{III}) compounds in which the lanthanide cations presented an eight coordination number, too.

Later Mialane [24] showed that change in size of Ln^{III} ions in 1:1 polyoxometalate complexes means that homologous compounds with noticeably different radii may differ in structure.

Recently it was demonstrated that nano-sized polyoxometallolanthanoates, such as $[Pr_6Mo_{120}]$ [25],

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$[Eu_4Mo_{128}]$ [26] or $[Ce_{16}W_{148}]$ [27] can be constructed through the coordination of Ln^{III} ions by the outer oxygen atoms of polyoxometalate anions.

Wassermann [28] synthesized several new large polyoxotungstates $[Ln_3As_4W_{140}]$ and $[Ln_4As_4W_{140}]$ by reaction of lanthanide cations with well-known 'As_4W_{40}' anions. In these complexes the lanthanide cations are eight or nine coordinated to oxygen atoms (distorted square antiprism or distorted monocapped square antiprism environment).

Yamase [29] synthesized the first examples of polyoxometallolanthanoates with a crown-shaped ring structure that encapsulates a single alkali-metal cation in the center ($[M \subset \{Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})\}_x]^{y-}$, $M = K^+$, Cs^+, $x = 6$ or 4 and $y = 35$ or 23). The coordination numbers 8 and 9 are also commonly found in these compounds, in which the La^{III} ions are used as linkers.

However, the first complex of trilacunary Keggin with lanthanide ions was reported by Knoth in 1986 [30]. This complex has a sandwich-type structure consisting of two $[PW_9O_{34}]^{9-}$ (**PW$_9$**) units connected by a belt of three lanthanide atoms. The belt contains three oxygen atoms, alternating with the three lanthanide atoms. The cerium(IV) derivative revealed the presence of two types of cerium(IV) ions, one being six-coordinated while the other two are seven-coordinated (Fig. 1).

Herein the synthesis and characterisation of two new lanthanide complexes $[\{Ln_3O_3(OH_2)_2\}(PW_9O_{34})_2]^{15-}$ where $Ln^{III} = Ce$, La (**Ln^{III}PW$_9$**) of the trilacunary $[PW_9O_{34}]^{9-}$ (**PW$_9$**) polyoxometalate are reported. The results of research suggest a sandwich-type structure similar to the structure of the Ce^{IV} complex reported by Knoth et al. [30].

2. Experimental

2.1. Materials and methods

Reagent grade chemicals were used and all syntheses and studies were carried out in distilled water.

ICP was used for the elemental analysis of cerium, lanthanum, phosphorus and tungsten whereas flame-photometry was used for the elemental analysis of sodium. The water content was thermogravimetrically determined, by means of a Paulik Erdely OD-102 type derivatograph in a temperature range of 20–600 °C, using a heating rate of 5 °C min^{-1}. The conductometric studies were performed on a Radelkis OK-102 type conductometer, in acetate buffer (pH 5), using different Ln:PW$_9$ molar ratios.

UV–Vis spectra were recorded on a Perkin–Elmer Lambda 19 spectrometer using Teflon-stoppered quartz cells with a path length of 1 cm. A FTIR-JASCO 610 spectrophotometer was used to record IR spectra for samples pelleted in KBr. Raman experiments were performed on solid powders at room temperature, using a JOBIN-YVON LABRAM Raman spectroscope equipped with a microscope, CCD detection and a 632.8 nm (red) line of a He–Ne laser with a power of 1–5 mW. ^{31}P (121.5 MHz) NMR spectra of saturated solutions were recorded at room temperature on a Bruker AC-300 MHz spectrometer. Chemical shifts were referenced to 85% H_3PO_4. The main parameters used were 32K data domain size, 62 500 Hz spectral width, 2 s relaxation delay and 100 scans. ES-MS spectra were recorded on a TSQ 7000 Finnigan MAT mass spectrometer operating in the negative ion mode. Instrument parameters were adjusted for optimum results. The following settings were utilized: ESI spray voltage: 4.5 kV; sheath gas pressure (N_2): 35 ψ; capillary temperature: 200 °C.

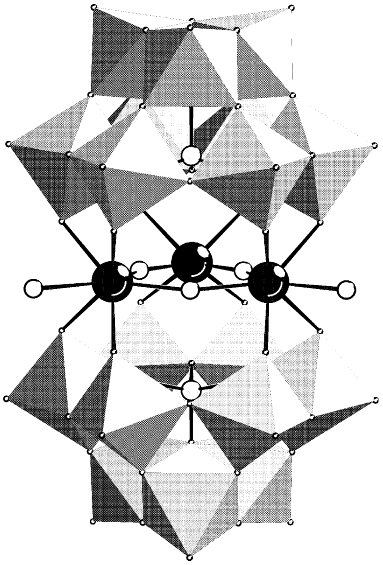

Fig. 1. Proposed structure of lanthanide complexes of trilacunary $Na_8[HPW_9O_{34}]$ polyoxometalate.

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 ($F = 5$ 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 ($NaHPO_4$–H_3PO_4) buffer solutions (pH 3–5.5). pH measurements were carried out using a digital pH-meter (MV-Pr™citronic, GDR) equipped with a combined glass electrode (Metrohm, Switzerland). For each measurement a 6×10^{-3} M $Ln^{III}PW_9$ solution (2 ml) was dissolved in the buffer solution (10 ml).

2.1.1. Ion exchange chromatography

Degassed water (50 ml) was added to the strongly acidic macroreticular resin (10 g), Vionit CS3 (H ~ form; P–SO_3H where P = macroreticular polymer).

The resin was swirled for a while and water was removed by decanting. The process was repeated until the aqueous phase was clear and colourless. The resin was then packed into a column (27 cm × 1 cm; length × diameter). A solution of 4% NaOH was then eluted through the column, followed by distilled water. The resulting P–SO_3Na column was washed five times with distilled water (50 ml). A solution of **Ce^{III}PW$_9$** or **La^{III}PW$_9$** (0.5 g) in H_2O (10 ml) was loaded onto the column. The eluant was collected and the solvent removed by evaporation. The lanthanide complexes appeared unchanged (by FT-IR spectroscopy). An anion exchange column of identical size was packed with strongly basic resin, Amberlyst A-27 (Cl form; P–$NR_3^+Cl^-$). A sample of **Ce^{III}PW$_9$** or **La^{III}PW$_9$** was loaded onto the column in a manner similar to that described for the cation exchange resin. All samples were retained on the upper half of the column.

2.2. Complex preparation

The sodium salt of the polyoxometalate ligand, $Na_8H[PW_9O_{34}]$ (**PW$_9$**), was prepared as described before [31].

2.2.1. Preparation of $Na_{12}H_3[\{La_3O_3(OH_2)_2\}(PW_9O_{34})_2]\cdot 18H_2O$

$LaCl_3\cdot 7H_2O$ (1.11 g, 3 mmol) was dissolved in water (10 ml) and added dropwise, while stirring, to an aqueous solution (50 ml) of $Na_8H[PW_9O_{34}]$ (5 g, 2.04 mmol). The slightly turbid final solution was refluxed for 1 h, its pH adjusted to 5 with 6 M HCl and then filtered under suction. The filtrate was heated at 80 °C, while stirring, until half the volume remained. It was then cooled to room temperature. A few days later a white precipitate appeared. It was recrystallized with hot water, at pH 5 and dried under vacuum over P_2O_5. The yield was 2.1 g (37.30%). *Anal.* Calc. for $H_{43}La_3Na_{12}O_{91}P_2W_{18}$ (5562.94): La 7.49; Na 4.95; P 1.11; W 59.48%. Found: La 7.23; Na 5.16; P 1.07; W 59.62%. IR (polyoxometalate region, cm^{-1}): 1092, 1049, 1009, 974, 953, 889, 837, 798, 769, 732, 594, 505, 482. Raman (cm^{-1}): 985, 970, 940, 897, 866, 515, 219, 130. ^{31}P NMR (D_2O) $\delta -10.93$ (s).

2.2.2. Preparation of $Na_{12}H_3[\{Ce_3O_3(OH_2)_2\}(PW_9O_{34})_2]\cdot 45H_2O$

$CeCl_3\cdot 7H_2O$ (1.11 g, 3 mmol) was dissolved in water (10 ml) and added dropwise, while stirring, to an aqueous solution (50 ml) of $Na_8H[PW_9O_{34}]$ (5 g, 2.04 mmol). The resulting solution was refluxed for 1 h, the pH adjusted to 5 using 6 M HCl and then filtered under suction. The filtrate was heated at 80 °C, while stirring, until half its volume remained. After a few days at room temperature a brown powder precipitated. It was recrystallized with hot water, at pH 5 and dried under vacuum over P_2O_5. The complex was recrystallized with hot water, at pH 4.5–5. The yield was 2.7 g (44.12%). *Anal.* Calc. for $H_{97}Ce_3Na_{12}O_{118}P_2W_{18}$ (6052.99): Ce 6.94; Na 4.55; P 1.02; W 54.66%. Found: Ce 6.75; Na 4.69; P 1.00; W 54.75%. IR (polyoxometalate region, cm^{-1}): 1091, 1051, 1015, 972, 953, 895, 840, 800, 783, 731, 592, 511, 474. Raman (cm^{-1}): 961, 937, 893, 838, 806, 554, 430, 363, 214, 173, 143. ^{31}P NMR (D_2O) $\delta -9.67$ (s).

2.2.3. Preparation of $Cs_{12}H_3[\{Ce_3O_3(OH_2)_2\}(PW_9O_{34})_2]\cdot 25H_2O$

CsCl (1 g, 5.94 mmol) was added under stirring to a hot solution (pH 4.5–5) obtained by dissolving 1 g (0.165 mmol) $Na_{12}H_3[\{Ce_3O_3(OH_2)_2\}(PW_9O_{34})_2]\cdot 45H_2O$ in 20 ml of water. Then the solution was left to cool at room temperature. After several hours, a brown precipitate was formed. The product was recrystallized using hot water. *Anal.* Calc. for $H_{57}Ce_3Cs_{12}O_{98}P_2W_{18}$ (7011.67): Ce 5.99; Cs 22.74; P 0.88; W 47.19%. Found: Ce 5.89; Cs 22.81; P 0.81; W 47.31%.

3. Results and discussion

In order to establish the complexes composition in solution, conductometric titrations of PW$_9$ solution with Ln^{3+} ions were performed. The titration results showed a breakpoint at 3:2 **Ln^{III}**:**PW$_9$** ratio (Fig. 2).

The pH range, in which the **Ce^{III}PW$_9$** complex is formed was determined by spectrophotometry ($\lambda = 470$ nm) of some **Ce^{III}**:**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. The

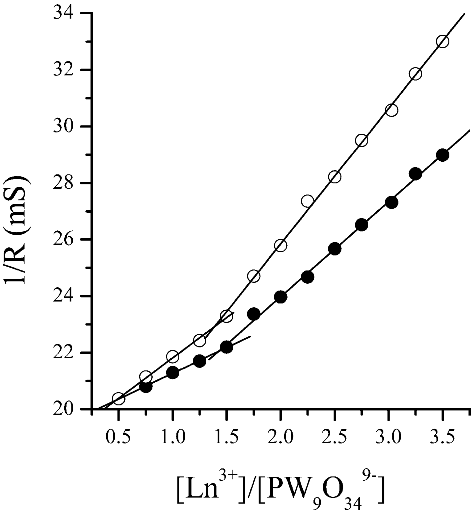

Fig. 2. Conductometric titrations of trilacunary PW$_9$ anion with lanthanide ions.

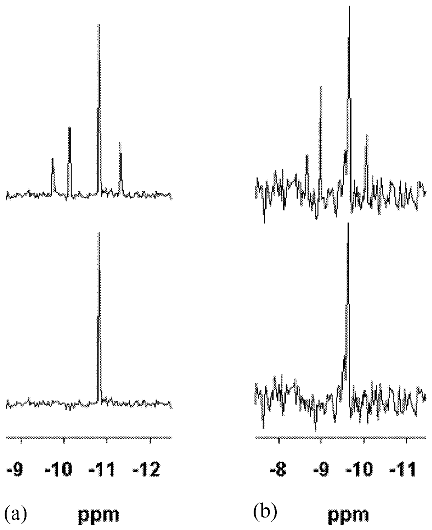

Fig. 3. (a) ^{31}P NMR spectra of $\mathbf{La^{III}PW_9}$ (a) and $\mathbf{Ce^{III}PW_9}$ (b); when the reaction occurs at room temperature (up) and after being refluxed for 1 h (down).

same value of pH was taken into account during the synthesis of the complex $\mathbf{La^{III}PW_9}$.

We have studied the influence of temperature on the formation reactions of the complexes $\mathbf{La^{III}PW_9}$ and $\mathbf{Ce^{III}PW_9}$ by ^{31}P NMR spectroscopy.

The solid products separated by the reactions of lanthanide cations and the $\mathbf{PW_9}$ polyoxometalate at room temperature, dissolved in water, display in the ^{31}P NMR spectra four signals of various intensity attributed to some mixtures of various species (Fig. 3(up)). After the 1 h reflux of the reaction mixtures, the ^{31}P NMR spectra present one single signal (Fig. 3(down)), which shows the presence of one compound.

When the complex $\mathbf{Ce^{III}PW_9}$ is dissolved in water, the pH of solution is raised from 5 to 7.5–8 by adding a dilute solution of sodium hydroxide, and the solution is stirred, the colour fades, which indicates the decomposition of the complex.

When a solution of $\mathbf{Ce^{III}PW_9}$ or $\mathbf{La^{III}PW_9}$ was loaded onto the sodium form (P–$SO_3^-Na^+$) of the cation-exchange column, no retention of the $\mathbf{Ce^{III}PW_9}$ or $\mathbf{La^{III}PW_9}$ complexes was observed. The FT-IR spectrum of each individual eluant confirmed the integrity of the eluted parent complexes, $\mathbf{Ce^{III}PW_9}$ or $\mathbf{La^{III}PW_9}$. In a second series of experiments, $\mathbf{Ce^{III}PW_9}$ or $\mathbf{La^{III}PW_9}$ was loaded onto an anion-exchange column in its Cl form, P–$NR_3^+Cl^-$. In this case, both anionic complexes were retained on the column. Control experiments were carried out with aqueous solutions of $CeCl_3$ and $LaCl_3$. As expected, the lanthanide cations were retained on the cation-exchange column but passed through the anion-exchange column. Consequently, these simple ion-exchange experiments provide good evidence for inner-sphere bonding of the lanthanide cations to $\mathbf{PW_9}$ [32].

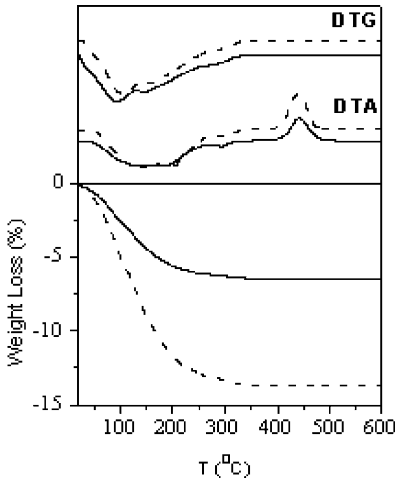

Fig. 4. Thermogravimetric and thermodifferential curves of $\mathbf{La^{III}PW_9}$ (solid) and $\mathbf{Ce^{III}PW_9}$ (dashed).

The study of the La(III) and Ce(III) polyoxometalate sodium salts' thermal behavior reveals that the complexes contain 20 and 47 water molecules, respectively. Four main processes, three endothermal and one exothermal were observed on the DTA curve of both complexes (Fig. 4). The endothermal processes at ~100–120, ~160–200, ~250–300 °C were assigned to water loss. The DTG curves showed that the second process is the fastest and the third process, where the two coordination water molecules are lost, is the slowest. The exothermal process, with a maximum at ~520 °C on the DTA curve, was assigned to the decomposition of the polyoxometalates [33]. On the basis of the thermogravimetric studies it can be thus concluded that $\mathbf{La^{III}PW_9}$ and $\mathbf{Ce^{III}PW_9}$ are thermally stable up to 350 °C.

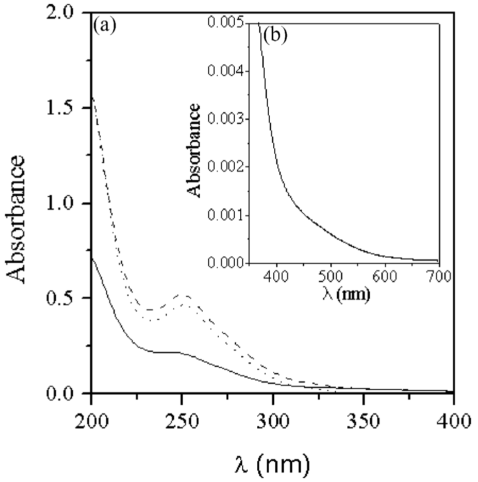

Fig. 5. (a) UV spectra of the sodium salts of $\mathbf{La^{III}PW_9}$ (dashed), $\mathbf{Ce^{III}PW_9}$ (dotted) and PW_9 (solid) obtained in 1×10^{-5} mol l^{-1} aqueous solution; (b) visible spectrum of $\mathbf{Ce^{III}PW_9}$ obtained in 1×10^{-3} mol l^{-1} aqueous solution.

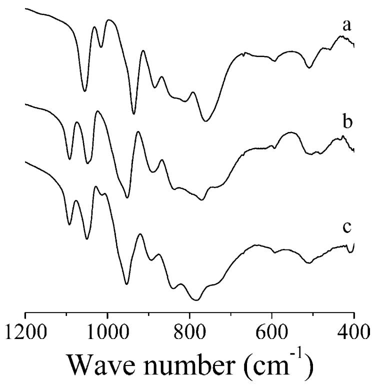

Fig. 6. FT-IR spectra of PW_9 (a), **La^{III}PW$_9$** (b) and **Ce^{III}PW$_9$** (c) recorded in KBr pellets.

3.1. *Electronic spectroscopy*

The UV-electronic spectra of the **PW$_9$** ligand and **Ln^{III}PW$_9$** complexes (Fig. 5) exhibit two characteristic bands at ~200 and ~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) [34]. 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 $Ce^{III}PW_9$ complex exhibits an additional metal-to-ligand charge transfer band at ~470 nm [35].

3.2. *Vibrational spectroscopy*

When comparing the IR spectra of **La^{III}PW$_9$** and **Ce^{III}PW$_9$** polyoxometalate complexes with that of the **PW$_9$** ligand, a shift of the stretching vibrations appearing in the 1200–700 cm^{-1} range towards higher frequencies is observed (Fig. 6). This is consistent with an increase of the anion cohesion when coordination of the lanthanide ions in the polyoxometalate framework takes place [36]. In the range 1000–700 cm^{-1} three characteristic bands were observed and assigned to the asymmetric stretching vibrations of the bridges ($W-O_b-W$) and of the terminal bonds ($W-O_t$) [36,37]. The splitting of the characteristic P–O asymmetric stretching vibration between 1100 and 1000 cm^{-1} suggests a decrease in the PO_4 group symmetry by coordination of the lanthanide ions to the ligand [37]. The lack of the P=O band above 1100 cm^{-1} in the infrared spectra of the **PW$_9$** ligand and **Ln^{III}PW$_9$** polyoxometalate complexes proves that these have A-type structures and therefore the preservation of the **A-PW$_9$** fragments in the **La^{III}PW$_9$** and **Ce^{III}PW$_9$** complexes [38].

It is also important to notice that, for the Raman investigations, the vibration bands of **Ln^{III}PW$_9$** polyoxometalate complexes shift towards higher energies providing evidence for an increase in polyoxometalate stability (Fig. 7) [39]. Raman spectra of **Ln^{III}PW$_9$** polyoxometalates show characteristic strong vibration bands at ~985, ~970 and ~220 cm^{-1}, assigned to $\nu_s(W-O_t)$, $\nu_{as}(W-O_t)$ and $\nu_s(W-O_i)$, respectively, where O_i represents the bridging oxygen between the internal phosphorus heteroatom and tungsten addenda [39]. Other weak lines are $\nu_s(P-O_i)$, ~1020, $\nu_{as}(P-O_i)$, ~950, $\nu_{as}(W-O_b)$ ~900 and 850 cm^{-1} [39]. In the spectrum of **Ce^{III}PW$_9$**, the last two bands become one broad band.

Table 1
^{31}P NMR chemical shifts for some sandwich type complexes of $[PW_9O_{34}]^{9-}$

Polyoxometalate	Δ (ppm)	References
$[(CeO)_3(H_2O)_2(PW_9O_{34})_2]^{12-}$	−7.57	[23]
$[(CeO)_3(H_2O)_2(PW_9O_{34})_2]^{15-}$	−9.67	
$[(LaO)_3(H_2O)_2(PW_9O_{34})_2]^{15-}$	−10.93	
$[(MeSnOH)_3(PW_9O_{34})_2]^{12-}$	−10.06	
$[(BuSnOH)_3(PW_9O_{34})_2]^{12-}$	−10.12	[32]
$[(PhSnOH)_3(PW_9O_{34})_2]^{12-}$	−10.9	[32]
$[Sn_3^{II}(PW_9O_{34})_2]^{12-}$	−12.00	[33]
$[(HOSnOH)_3(PW_9O_{34})_2]^{12-}$	−11.50	[33]

3.3. ^{31}P *NMR spectroscopy*

The ^{31}P NMR spectra (Fig. 3(down)) show one singlet for both lanthanide complexes. The values for the chemical shifts are similar to the values observed for other 3:2 sandwich complexes of PW_9 (Table 1). The resonances observed for both Ce(III) and La(III) complexes are shifted toward higher fields when compared to the Ce(IV) complex. This is due to the higher negative charge of the heteropolyanions.

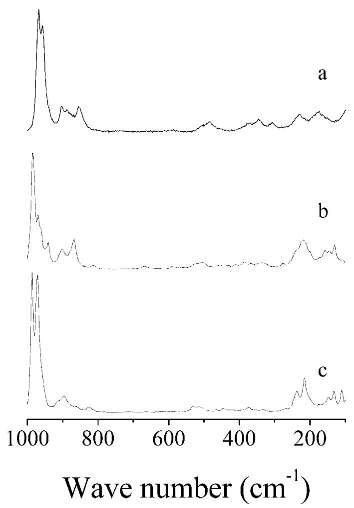

Fig. 7. Raman spectra of PW_9 (a), **La^{III}PW$_9$** (b) and **Ce^{III}PW$_9$** (c).

Table 2
Electrospray ionization mass spectral data for $Na_{12}H_3[(LaO)_3(OH_2)_2(PW_9O_{34})_2]\cdot 18H_2O$ and $Cs_{12}H_3[(CeO)_3(H_2O)_2(PW_9O_{34})_2]\cdot 25H_2O$

Species of 3^- charge state	m/z	Species of 4^- charge state	m/z	Species of 5^- charge state	m/z
$Na_{12}[(LaO)_3(H_2O)_2(PW_9O_{34})_2]^{3-}$	1745	$Na_{11}[(LaO)_3(H_2O)_2(PW_9O_{34})_2]^{4-}$	1303	$Na_{10}[(LaO)_3(H_2O)_2(PW_9O_{34})_2]^{5-}$	1038
$Na_{11}H[(LaO)_3(H_2O)_2(PW_9O_{34})_2]^{3-}$	1738	$Na_{10}H[(LaO)_3(H_2O)_2(PW_9O_{34})_2]^{4-}$	1298	$Na_9H[(LaO)_3(H_2O)_2(PW_9O_{34})_2]^{5-}$	1033
$Cs_{12}[(CeO)_3(H_2O)_2(PW_9O_{34})_2]^{3-}$	2186	$Cs_{11}[(CeO)_3(H_2O)_2(PW_9O_{34})_2]^{4-}$	1606	$Cs_{10}[(CeO)_3(H_2O)_2(PW_9O_{34})_2]^{5-}$	1258
$Cs_{11}H[(CeO)_3(H_2O)_2(PW_9O_{34})_2]^{3-}$	2142	$Cs_{10}H[(CeO)_3(H_2O)_2(PW_9O_{34})_2]^{4-}$	1573	$Cs_9H[(CeO)_3(H_2O)_2(PW_9O_{34})_2]^{5-}$	1232
Species of 6^- charge state	m/z	Species of 7^- charge state	m/z	Species of 8^- charge state	m/z
$Na_9[(LaO)_3(H_2O)_2(PW_9O_{34})_2]^{6-}$	861	$Na_8[(LaO)_3(H_2O)_2(PW_9O_{34})_2]^{7-}$	735	$Na_7[(LaO)_3(H_2O)_2(PW_9O_{34})_2]^{8-}$	640
$Na_8H[(LaO)_3(H_2O)_2(PW_9O_{34})_2]^{6-}$	857	$Na_7H[(LaO)_3(H_2O)_2(PW_9O_{34})_2]^{7-}$	732	$Na_6H[(LaO)_3(H_2O)_2(PW_9O_{34})_2]^{8-}$	637
$Cs_9[(CeO)_3(H_2O)_2(PW_9O_{34})_2]^{6-}$	1026	$Cs_8[(CeO)_3(H_2O)_2(PW_9O_{34})_2]^{7-}$	860	$Cs_7[(CeO)_3(H_2O)_2(PW_9O_{34})_2]^{8-}$	736
$Cs_8H[(CeO)_3(H_2O)_2(PW_9O_{34})_2]^{6-}$	1004	$Cs_7H[(CeO)_3(H_2O)_2(PW_9O_{34})_2]^{7-}$	842	$Cs_6H[(CeO)_3(H_2O)_2(PW_9O_{34})_2]^{8-}$	720

3.4. Electrospray mass spectrometry

Polyoxoanions are highly negatively charged molecules and form adducts with cations, such as Cs^+ and H^+, in this case [40]. Thus, different charge states can be formed. The ES mass spectrum of $Cs_{12}H_3[(CeO)_3(H_2O)_2(PW_9O_{34})_2]\cdot 25H_2O$, taken in water and displayed in Fig. 8, shows the 3^-, 4^-, 5^-, 6^-, 7^- and 8^- charge regions.

The negative ion ESI mass spectra of the aqueous solution of **La^{III}PW$_9$** and **Ce^{III}PW$_9$** are shown in Table 2. Several clusters of peaks arising from differently charged lanthanide complexes are present in the spectra, the multiple nature of each peak being due to the five naturally occurring isotopes of tungsten.

The peak at m/z 2186 is attributed to the parent ion $Cs_{12}[\{Ce_3O_3(OH_2)_2\}(PW_9O_{34})_2]^{3-}$, while the peak at m/z 2142 results from the parent ion when loosing one cesium atom and at the same time gaining one proton atom. Loss of an extra Cs atom with addition of an extra proton gives the peak at m/z 2098. This successive loss of Cs atoms and addition of protons continues up to the cesium free triply charged negative ion $H_{12}[\{Ce_3O_3(OH_2)_2\}(PW_9O_{34})_2]^{3-}$, which appears at m/z 1658. A similar behavior is observed for **La^{III}PW$_9$**.

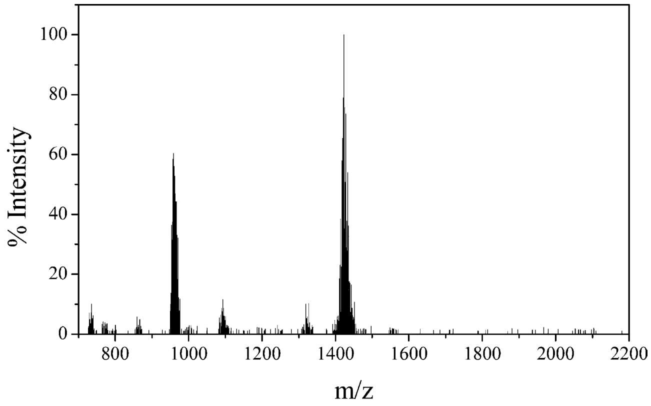

Fig. 8. ES mass spectrum of $Cs_{12}H_3[(CeO)_3(H_2O)_2(PW_9O_{34})_2]\cdot 25H_2O$, taken in water.

3.5. Electrochemical behavior

The electrochemical behavior of compounds (**I**) and (**II**) was investigated in comparison with that of the **PW$_9$** ligand (Table 3).

The electrochemical response of **Ce^{III}PW$_9$** consists of two successive redox peak pairs in the negative potential range and another two in the positive range (Fig. 9). Peaks I and II were assigned to two tungsten-centered single electron redox processes [41], while peaks I′ and II″, correspond to two single electron cerium-centered processes. The existence of two waves for the Ce^{3+}/Ce^{4+} redox couple could be explained by the nonequivalence of the Ce atoms in the polyoxotungstate molecule, where one Ce atom is six coordinated and two are seven coordinated.

Table 3
CV data for the lanthanide complexes of trilacunary $Na_8[HPW_9O_{34}]$ polyoxometalate

Process	E_{pa} (V)	E_{pc} (V)	$\varepsilon^{0'}$ (V)	ΔE_p (V)
$Na_8[HPW_9O_{34}]\cdot 20H_2O$				
I	−0.705	−0.793	−0.749	0.088
II	−0.903			
$Na_{12}H_3[(LaO)_3(OH_2)_2(PW_9O_{34})_2]\cdot 18H_2O$				
I	−0.73	−0.873	−0.8015	0.143
II	−0.911	−1.012	−0.9615	0.101
$Na_{12}H_3[(CeO)_3(OH_2)_2(PW_9O_{34})_2]\cdot 45H_2O$				
I′	0.498	0.548	0.523	0.050
II′	0.355	0.337	0.346	0.018
I	−0.791	−0.862	−0.826	0.071
II	−0.928	−1.016	−0.972	0.088

E_{pa}, oxidation potential; E_{pc}, reduction potential; $\varepsilon^{0'}$, formal standard potential estimated as the average of anodic and cathodic peak potentials; ΔE_p the difference between the redox peak potentials. Experimental conditions: H_3PO_4–Na_2HPO_4 buffer solution; pH 4.0, 25 °C; graphite working electrode; scan rate 100 mV s^{-1}; $c = 1.28 \times 10^{-3}$ M, potentials recorded vs SCE.

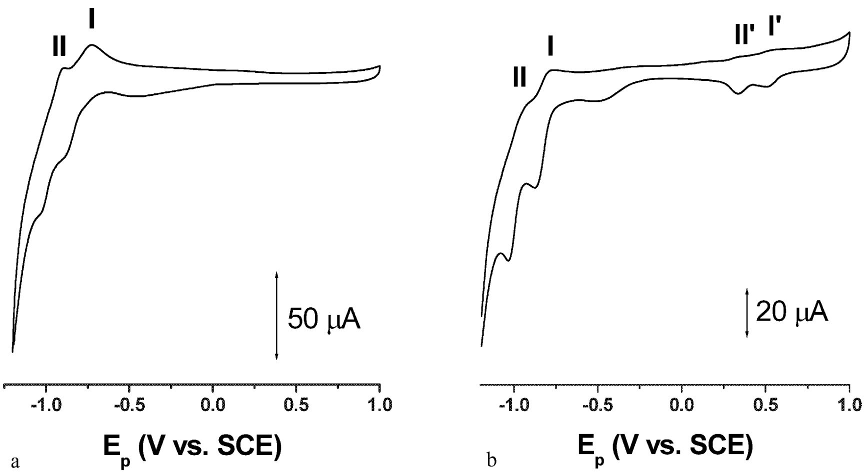

Fig. 9. Cyclic voltammograms of **La^{III}PW$_9$** (a) and **Ce^{III}PW$_9$** (b) recorded in H_3PO_4–Na_2HPO_4 pH 4.0 buffer solution, scan rate 50 mV s^{-1}, $c = 1.28 \times 10^{-3}$ M.

In the case of La^{III}PW$_9$, only the two waves corresponding to the polyoxotungstate framework were observed, as it was expected. The cyclic voltammogram was very similar to that of the parent anion, indicating a lack of influence by the lanthanum atom present in the polyoxometalate molecule.

The behavior of the corresponding half-wave potentials ($E_{1/2}$) is also indicative of the complexes electrochemical properties (as the half-wave potential for a reversible wave is close to the formal potential $\varepsilon^{0'}$) [42]. A slight negative shift of the corresponding half-wave potentials ($E_{1/2}$) is observed due to the coordination of the lanthanide cations. It is noteworthy to mention that in the presence of Ce, a slight positive shift of the formal standard potentials $\varepsilon^{0'}$ for the tungsten-centered redox processes is evident, when compared to those of the La complex (Table 3).

The linear relationships between peak currents and the square root of the scan rates for the cathodic peak I provide evidence for a diffusion controlled process (Fig. 10) [42].

The change of the pH exhibits minor variations in the formal standard potential $\varepsilon^{0'}$ (estimated as the average of anodic and cathodic peak potentials) for increasing values of pH (Fig. 11).

The formal standard potential, $\varepsilon^{0'}$, exhibits a linear dependence upon pH. The slopes varying between -0.001 and -0.01349 mV (ΔpH)$^{-1}$ imply that protons are not involved in all the redox processes.

4. Conclusion

Two new heteropolyoxometalate complexes $[\{Ln_3O_3(OH_2)_2\}(PW_9O_{34})_2]^{15-}$ were synthesized by reaction of Ln(III) ions with the trilacunary Keggin 9-tungstophosphate, after establishing the reaction stoichiometry. Spectroscopic studies suggest that both have

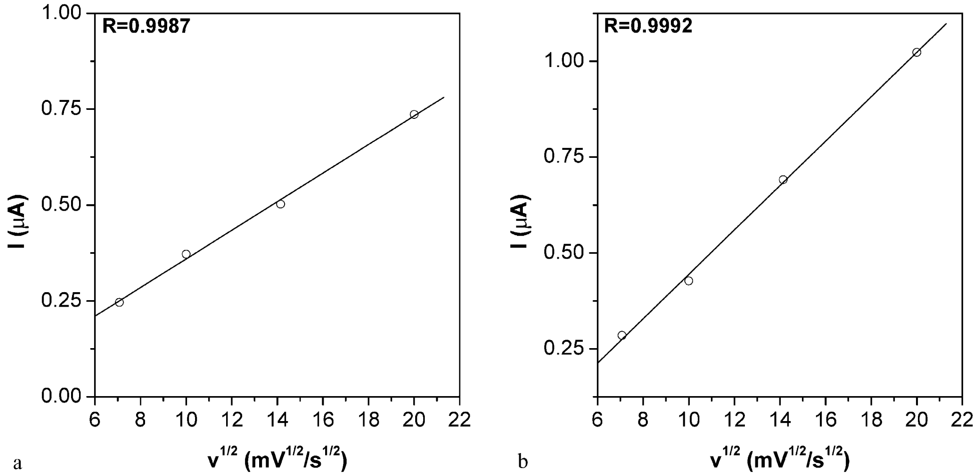

Fig. 10. Dependence of the cathodic peak I current on the scan rate for $Na_{12}H_3[(LaO)_3(OH_2)_2(PW_9O_{34})_2]\cdot 18H_2O$ (a) and $Na_{12}H_3[(CeO)_3(OH_2)_2(PW_9O_{34})_2]\cdot 45H_2O$ (b).

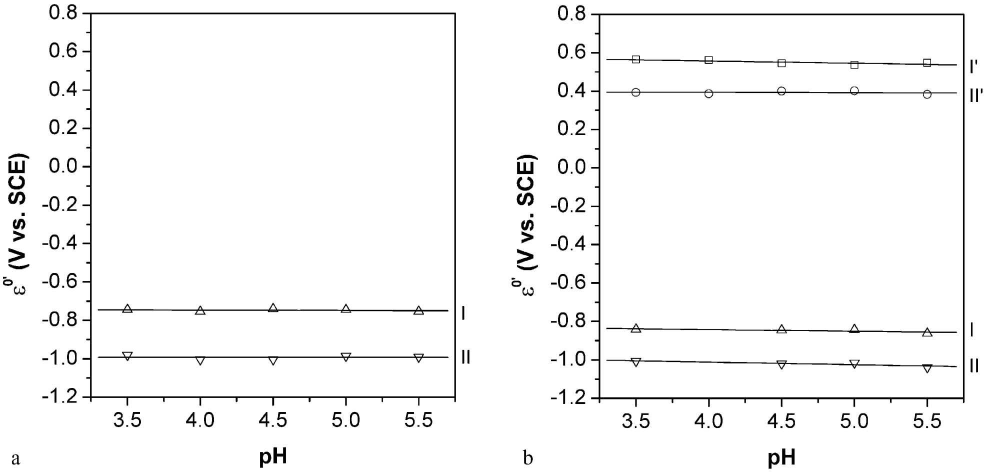

Fig. 11. Dependence of the formal standard potentials on the pH for $Na_{12}H_3[(LaO)_3(OH_2)_2(PW_9O_{34})_2]\cdot 18H_2O$ (a) and $Na_{12}H_3[(CeO)_3(OH_2)_2(PW_9O_{34})_2]\cdot 45H_2O$ (b).

a sandwich-type structure (Fig. 1), similar to the structure of the Ce(IV) complex reported by Knoth et al., [30]. The electrochemical behavior of the two lanthanide derivatives of **PW_9** illustrates the influence exerted by the secondary heteroatoms, Ce and La, upon the redox character of the **PW_9** lacunary anion. Furthermore, evidence has been presented for the nonequivalence of the Ce atoms in the polyoxotungstate structure of **$Ce^{III}PW_9$**. This is principally reflected in the formal standard potential values of the tungsten-centered redox processes. The redox behavior of the newly synthesized Ce derivative recommends it as a promising mediator (electrocatalyst) in indirect electrochemical reactions.

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