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Dedicated to professor Gh. Marcu at his 80th anniversary

ELECTROCHEMICAL CHARACTERIZATION OF SANDWICH-TYPE PHOSPHOTUNGSTOCERATE (IV) AND ARSENOTUNGSTOCERATE (IV) IN AQUEOUS AND NON-AQUEOUS SOLUTION

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ABSTRACT. The electrochemical properties of two sandwich-type polyoxotungstocerate (IV) $[(CeO)_3(H_2O)_2(PW_9O_{34})_2]^{12-}$ and $[(CeO)_3(H_2O)_2(AsW_9O_{34})_2]^{12-}$ have been studied by cyclic voltammetry in aqueous and acetonitrile solutions. Voltammograms recorded in aqueous solutions showed the existence of two waves for the Ce(III)/Ce(IV) redox couple. These could be explained by a nonequivalence of the Ce atoms in the polyoxotungstate molecule, where one Ce atom is six coordinated and the other two, are seven coordinated. The presence of only one peak pair for Ce(III)/Ce(IV) suggests the equivalence of these metal ions in the polyoxometalate complexes when isolated as tetrabutylammonium salts. When increasing amounts of $LiClO_4$ have been added to the acetonitrile solutions of the polyoxotungstocerate while keeping the ionic strength constant with 1M $[Bu_4N]ClO_4$ a dramatic change of the electrochemical behavior was observed, which was assigned to the association of Li^+ ions with the reduced forms of the polyoxometalates.

Introduction

The interest regarding the polyoxometalates chemistry has increased enormously in last decades when a very large number of different structures as well as new potential applications of such compounds have been reported [1-8]. On this context, it is recognized that the different coordination geometries of the lanthanide cations and the vacant sites afforded by the polyoxometalates usually result in large oxometalate clusters [4-24], showing very interesting electroluminiscence and photoluminiscence activity [4, 11-14, 16, 22] as well as enhanced efficiency against HIV [25, 26].

One example of such compound, in which lanthanides act as linkers between trilacunary Keggin polyoxometalates was described for the first time by Knoth et al. in 1986 [27]. Its structure consists on a belt of three Ce alternating with three oxygens, sandwiched between two trilacunary 9-phosphotungstate units. In the belt, two of the cerium (IV) ions are 7 coordinated, and the third one is only 6 coordinated (Fig. 1).

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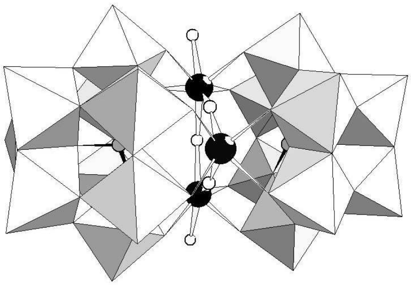

Fig.1. The polyhedral representation of the sandwich polyoxotungstocerates (WO_6 white octahedral; Ce – black spheres; P – grey spheres; O- white spheres).

Herein we report a detailed investigation of electrochemical behavior of $[(CeO)_3(H_2O)_2(PW_9O_{34})_2]^{12-}$ and its arsenic (V) derivative, in aqueous and non-aqueous solutions.

Experimental

1. Methods

Inductively Coupled Plasma Spectroscopy (I.C.P.) was used for the elemental analysis of tin and tungsten, and flamephotometry for sodium and potassium. The water content was thermogravimetrically determined, by means of a Paulik Erdely OD-102 type derivatograph at a temperature range of 20-600°C, using a heating rate of 5°C min^{-1}.

A Nicolet 5DX spectrophotometer was used to record the IR spectra of samples pelleted in KBr.

Cyclic voltammetry measurements were performed using a Vinci Technologies P/G STAT Z1 potentiostat, operating in conjunction with a 33120 A Hewlett Packard function /arbitrary waveform generator and with a Linseis LY 18100 X-Y recorder. A conventional (single-compartment) three electrode electrochemical cell was used, with a Metrohm planar platinum counter electrode and a reference electrode. For the aqueous solutions a Metrohm saturated calomel (Hg/Hg_2Cl_2) (SCE) was used as reference electrode, while for non-aqueous solution, a Metrohm Ag/AgCl electrode (a silver wire covered by AgCl, immersed in a saturated LiCl solution in acetonitrile, which was separated from the studied solution by a salt bridge of 0.1 M $[Bu_4N]ClO_4$ in acetonitrile). Pyrolytic graphite (Union Carbide, Φ~ 3mm) was used as a working electrode (WE). This was polished with emery paper 4000 and cleaned in an ultrasonicator, prior to use.

For aqueous solutions, the WE was polarized in a 10^{-3} M solution of the complex under study in phosphate buffer (pH = 4.0 - 5.5) with a scan rate between 50 and 400 mV s^{-1}.

For non-aqueous solutions, the WE was polarized in 10^{-3} M acetonitrile solution of the complex in the presence of 0.1 M $[Bu_4N]ClO_4$.

Solutions were deoxygenated using purified Ar gas (99.9%). While recording the voltammograms, Ar was passed over the solution surface.

2. Materials

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

The potassium salts $K_{10}H_2[(CeO)_3(H_2O)_2(PW_9O_{34})_2]\cdot18H_2O$ and $K_{10}H_2[(CeO)_3(H_2O)_2(AsW_9O_{34})_2]\cdot21H_2O$ have been prepared by the reported procedures [27, 28] and their purity have been proved by chemical analysis and IR spectra.

Synthesis of $[Bu_4N]_{10}H_2[(CeO)_3(PW_9O_{34})_2]$

To a solution of 1.0 g $K_{10}H_2[(CeO)_3(H_2O)_2(PW_9O_{34})_2]$ $18H_2O$ (0.176 mmol) in 30 mL hot water at pH= 4.5-5.0, 2.0 g $[Bu_4N]Br$ (6.204 mmol) were added under vigorous stirring. A pale yellow precipitate was formed, which was removed by vacuum filtration on G_3 frite, washed with 10 mL distilled water, dried under suction for 2 h and then over P_2O_5 for 24h. Yield: 1.23 g (95.45%).

Calcd. for: $[(C_4H_9)_4N]_{10}H_2[(CeO)_3(PW_9O_{34})_2]$ P: 0.84; W: 45.00; Ce: 5.71.

Found: P: 0.77; W: 45.22; Ce: 5.62.

Synthesis of $[Bu_4N]_{10}H_2[(CeO)_3(AsW_9O_{34})_2]$

To a solution of 1.0 g $K_{10}H_2[(CeO)_3(H_2O)_2(AsW_9O_{34})_2]$ $21H_2O$ (0.171 mmol) in 50 mL hot water at pH= 4.5-5.0, 2.0 g $[Bu_4N]Br$ (6.204 mmol) were added under vigorous stirring. A pale yellow precipitate was formed. which was removed by vacuum filtration on G_3 frite, washed with 10 mL distilled water, dried under suction for 2 h and then over P_2O_5 for 24h. Yield: 1.22 g (95.84%).

Calcd. for: $[(C_4H_9)_4N]_{10}H_2[(CeO)_3(AsW_9O_{34})_2]$ As: 2.01; W: 44.46; Ce: 5.65.

Found: As: 1.89; W: 44.61; Ce: 5.58.

Results and Discussions

The cyclic voltammograms of the $[(CeO)_3(H_2O)_2(XW_9O_{34})_2]^{12-}$ (X= P, As) complexes recorded in aqueous solutions at pH= 4.0 are depicted in Fig. 2.

Both complexes showed two successive redox peak pairs in the negative potential range, which were attributed to two single electron tungsten centered processes [29]. In this range, the cyclic voltammograms were very similar to that of the parent anion, indicating a lack of influence by the Ce(IV) present in the polyoxometalate framework. However a negative shift of the peaks provides proof for the coordination of the Ce(IV) to the trilacunary polyanions.

Two additional successive redox peak pairs appear in the positive range, which were assigned to two single electron cerium-centered processes [5]. The existence of two waves for the Ce(III)/Ce(IV) redox couple could be explained by the nonequivalence of the Ce atoms in the polyoxotungstate framework, where one Ce atom is six coordinated and the other two are seven coordinated [30].

The formal standard potentials $\varepsilon^{0'}$ (estimated as the average of anodic and cathodic peak potentials) of the tungstophosphate complex are negatively shifted by comparing with its tungstoarsenate analog (Table 1) which is in agreement with previous reports [31].

The positive shift of the formal standard potentials $\varepsilon^{0'}$ observed in Ce(IV) complexes when compared to the Ce(III) analogs [30], could be due to the lower negative charge of the Ce(IV) polyoxometalate complexes.

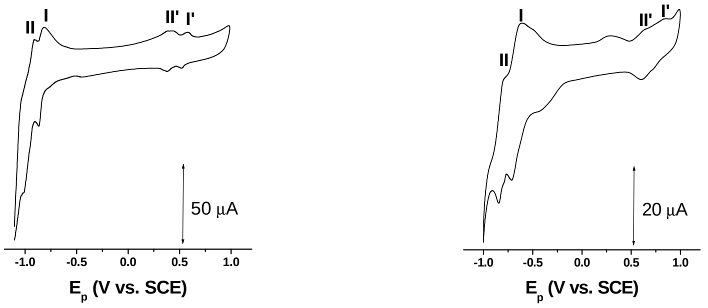

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Fig. 2. Cyclic voltammograms of $K_{10}H_2[(CeO)_3(OH_2)_2(PW_9O_{34})_2]\cdot18H_2O$ (a) and $K_{10}H_2[(CeO)_3(OH_2)_2(AsW_9O_{34})_2]\cdot21H_2O$ (b) recorded in aqueous solutions (pH= 4.0, v= 50 mV s^{-1}).

Table 1.

CV data for the $[(CeO)_3(H_2O)_2(XW_9O_{34})_2]^{12-}$ in aqueous solutions.

Process	$E_{p,a}$ (V)	$E_{p,c}$ (V)	$\varepsilon^{0'}$ (V)	ΔE_p (V)
$K_{10}H_2[(CeO)_3(OH_2)_2(PW_9O_{34})_2]\cdot18H_2O$				
I’	0.575	0.510	0.542	0.065
II’	0.399	0.379	0.389	0.020
I	-0.800	-0.852	-0.826	0.052
II	-0.921	-0.999	-0.960	0.078
$K_{10}H_2[(CeO)_3(OH_2)_2(AsW_9O_{34})_2]\cdot21H_2O$				
I’	0.812	0.738	0.775	0.074
II’	0.631	0.610	0.620	0.021
I	-0.619	-0.710	-0.664	0.091
II	-0.801	-0.836	-0.818	0.035

[a] 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℃; graphite working electrode; scan rate 100 mV·s^{-1}; c= 10^{-3}M, potentials recorded *vs* SCE.

The linear relationships between peak currents and the square root of the scan rates for redox waves I (Fig. 3) suggest the diffusion control of the electrochemical processes [32].

Changes in the pH resulted only in minor variations of the formal standard potential $\varepsilon^{0'}$, which imply that protons were not involved in the redox processes [30].

In order to investigate the influence of the different cations on the electrochemical behavior of the polyoxotungstocerate (IV) complexes, their tetrabutylammonium salts have been studied in acetonitrile solutions.

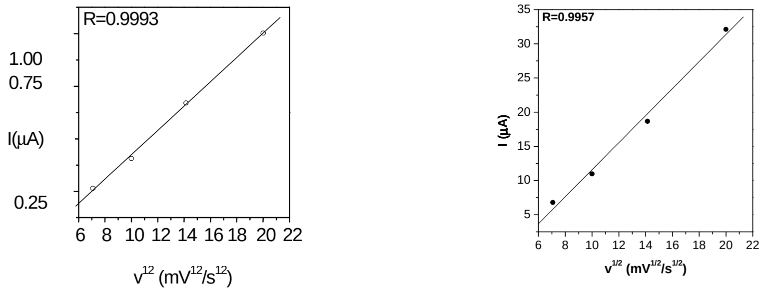

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Fig. 3. Dependence of the cathodic peak I current on the scan rate for: $K_{10}H_2[(CeO)_3(OH_2)_2(PW_9O_{34})_2]\cdot18H_2O$ (a) and $K_{10}H_2[(CeO)_3(OH_2)_2(AsW_9O_{34})_2]\cdot21H_2O$ (b) (pH=4.0).

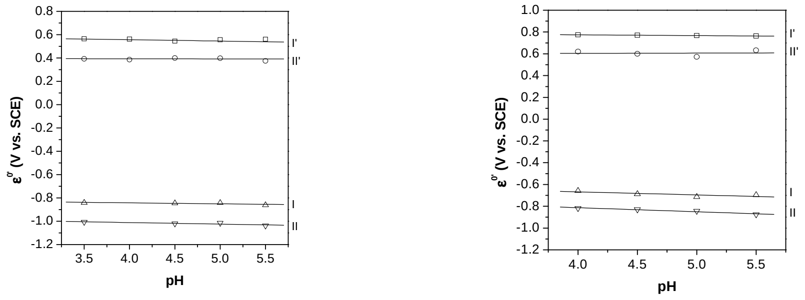

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Fig. 4. Dependence of the formal standard potentials on the pH for: $K_{10}H_2[(CeO)_3(OH_2)_2(PW_9O_{34})_2]\cdot18H_2O$ (a) and $K_{10}H_2[(CeO)_3(OH_2)_2(AsW_9O_{34})_2]\cdot21H_2O$ (b) (v= 100 mV s^{-1}).

When 0.1 M $[Bu_4N]ClO_4$ was used as supporting electrolyte, only one pair of waves were observed in the negative potential range for 9-tungstophosphate derivative, while the 9-tungstoarsenate analog exhibited two pair of peaks (Fig. 5). These were assigned to W(VI)/W(V) processes in the polyoxometalate framework. Both complexes, in acetonitrile solution showed only one peak pair in the positive potential range, due to the Ce(III)/Ce(IV) processes, suggesting equivalence of all the cerium ions present in the structure.

When increasing $LiClO_4$ quantities were added to the acetonitrile solutions of the polyoxometalates, while keeping the ionic strength constant at 0.1 by adding $[Bu_4N]ClO_4$, dramatic changes were observed in the voltammograms (Fig. 6). At high Li^+ concentrations, two additional peaks (II and III) appeared in the negative potential range, while the peaks I and I’ shifted to more positive values.

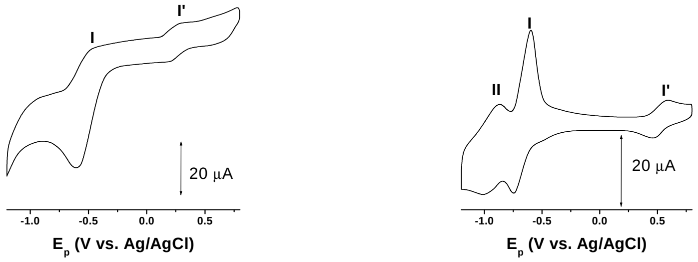

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Fig. 5. Cyclic voltammograms of $[Bu_4N]_{10}H_2[(CeO)_3(PW_9O_{34})_2]$ (a) and $[Bu_4N]_{10}H_2[(CeO)_3(AsW_9O_{34})_2]$ (b) (0.1 M $[Bu_4N]ClO_4$ in acetonitrile, v= 100 mV s^{-1}).

The positive shift of the peaks observed upon increasing the Li^+ concentration could be attributed to the association of Li^+ ions with the reduced forms of the polyoxometalates [33, 34].

Table 2.

CV data for the $[(CeO)_3(XW_9O_{34})_2]^{12-}$ in acetonitrile solutions.

Process	$E_{p,a}$ (V)	$E_{p,c}$ (V)	$\varepsilon^{0'}$ (V)	ΔE_p (V)
$[Bu_4N]_{10}H_2[(CeO)_3(PW_9O_{34})_2]$				
I’	0.212	0.268	0.265	0.056
I	-0.582	-0.470	-0.526	0.112
$[Bu_4N]_{10}H_2[(CeO)_3(AsW_9O_{34})_2]$				
I’	0.461	0.584	0.522	0.123
I	-0.744	-0.593	-0.668	0.151
II	-1.009	-0.865	-0.937	0.144

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: 0.1 M $[Bu_4N]ClO_4$ acetonitrile solution; 25°C; graphite working electrode; scan rate 100 mV·s^{-1}; c= 10^{-3}M, potentials recorded *vs* Ag/AgCl.

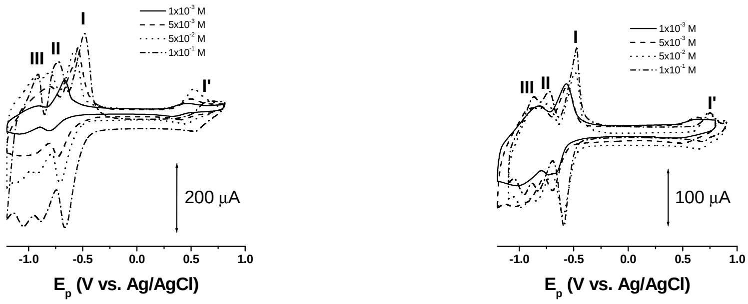

Fig. 6. Cyclic voltammograms of $[Bu_4N]_{10}H_2[(CeO)_3(PW_9O_{34})_2]$ (a) and $[Bu_4N]_{10}H_2[(CeO)_3(AsW_9O_{34})_2]$ (b) at different concentrations of $LiClO_4$ (0.1 M $[Bu_4N]ClO_4$ in acetonitrile, v= 100 mV s^{-1}).

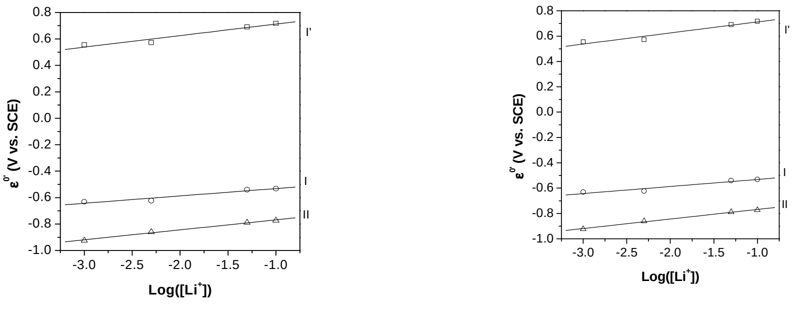

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Fig. 7. Dependence of the formal standard potentials on the Li$^+$ concentration for: $[Bu_4N]_{10}H_2[(CeO)_3(PW_9O_{34})_2]$ (a) and $[Bu_4N]_{10}H_2[(CeO)_3(AsW_9O_{34})_2]$ (b) (v= 100 mV s^{-1}).

The liniar relationships between the Log([Li$^+$]) and the formal standard potential $\varepsilon^{0'}$, with slopes of 0.078 (I'), 0.064 (I) and 0.096 (II) for the phosphotungstate derivative, and 0.087 (I'), 0.056 (I) and 0.075 (II) for its arsenotungstate analog, sugest that one Li$^+$ cation is envolved in each redox process, according to the following equations:

I': $[(Ce^{IV}O)_3(XW_9O_{34})_2]^{12-} + e^- + Li^+ \leftrightarrow Li[(Ce^{III}O)(Ce^{IV}O)_3(XW_9O_{34})_2]^{12-}$
I: $Li[(Ce^{III}O)(Ce^{IV}O)_3(XW_9O_{34})_2]^{12-} + e^- + Li^+ \leftrightarrow Li_2[(Ce^{III}O)(Ce^{IV}O)_3(XW_9O_{34})_2]^{12-}$
II: $Li_2[(Ce^{III}O)(Ce^{IV}O)_3(XW_9O_{34})_2]^{12-} + e^- + Li^+ \leftrightarrow Li_3[(Ce^{III}O)(Ce^{IV}O)_3(XW_9O_{34})_2]^{12-}$

Conclusions

The results of the performed investigations revealed that the electrochemical properties of the sandwich-type polyoxotungstocerate (IV) $[(CeO)_3(H_2O)_2(PW_9O_{34})_2]^{12-}$ and $[(CeO)_3(H_2O)_2(AsW_9O_{34})_2]^{12-}$ are different in aqueous and non-aqueous solution, suggesting different coordination of the cerium (IV) in aqueous and non-aqueous media. The addition of increasing amounts of the Li$^+$ cations results in a positive shift of the peaks which could be explained by the association of lithium ions with the reduced form of the polyoxotungstocerate.

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