

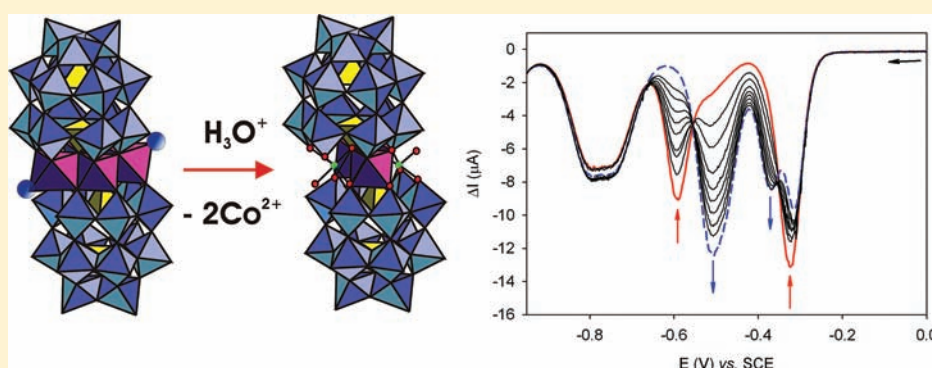
# Spectroscopic and Electrochemical Study of the Interconversion and Decomplexation of Cobalt(II) Sandwich Polyoxometalates Based on a Dawson-Type Anion

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**ABSTRACT:** The reaction of the trivalent Dawson polyoxometalate  $\alpha$ -[P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>]<sup>12-</sup> and the divalent cations Co<sup>2+</sup> is known to form a symmetrically derived sandwich complex of formula  $\beta\beta$ -[Co<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>)<sub>2</sub>]<sup>16-</sup> [symbolized as  $\beta\beta$ -Co<sub>4</sub>(P<sub>2</sub>W<sub>15</sub>)<sub>2</sub>] at low pH (ca. pH 3). We have shown previously that, by a slight modification of the reaction conditions, trinuclear  $\alpha\beta$ -[(NaOH<sub>2</sub>)Co<sub>3</sub>(H<sub>2</sub>O)(P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>)<sub>2</sub>]<sup>17-</sup> and dinuclear [(NaOH<sub>2</sub>)<sub>2</sub>Co<sub>2</sub>(P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>)<sub>2</sub>]<sup>18-</sup> complexes [symbolized as  $\alpha\beta$ -NaCo<sub>3</sub>(P<sub>2</sub>W<sub>15</sub>)<sub>2</sub> and Na<sub>2</sub>Co<sub>2</sub>(P<sub>2</sub>W<sub>15</sub>)<sub>2</sub>, respectively] can be synthesized as aqueous-soluble sodium salts.  $\alpha\beta$ -NaCo<sub>3</sub>(P<sub>2</sub>W<sub>15</sub>)<sub>2</sub> is a “lacunary” sandwich complex that can add a Co<sup>2+</sup> cation to form nearly quantitatively an unsymmetrical Dawson tetracobalt sandwich polyoxometalate,  $\alpha\beta$ -[Co<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>)<sub>2</sub>]<sup>16-</sup> [symbolized as  $\alpha\beta$ -Co<sub>4</sub>(P<sub>2</sub>W<sub>15</sub>)<sub>2</sub>]. Thus, for Co<sub>4</sub>(P<sub>2</sub>W<sub>15</sub>)<sub>2</sub>, the junctions between the trivalent {P<sub>2</sub>W<sub>15</sub>} subunits and the central tetrameric unit can be either both  $\beta$  type or  $\beta$  and  $\alpha$  types. The interconversion between  $\alpha\beta$ -Co<sub>4</sub>(P<sub>2</sub>W<sub>15</sub>)<sub>2</sub> and  $\beta\beta$ -Co<sub>4</sub>(P<sub>2</sub>W<sub>15</sub>)<sub>2</sub> and the decomplexation process at low pH, leading to the formation of  $\alpha\beta$ -NaCo<sub>3</sub>(P<sub>2</sub>W<sub>15</sub>)<sub>2</sub> and/or Na<sub>2</sub>Co<sub>2</sub>(P<sub>2</sub>W<sub>15</sub>)<sub>2</sub>, have been followed in aqueous solution at various pH values by electrochemistry, UV–visible absorption spectroscopy, and <sup>31</sup>P NMR spectroscopy.

## INTRODUCTION

In general, polyoxometalate anions exhibit varied structures, rich redox chemistry, photochemistry, and an ability to catalyze a wide range of industrially and biologically significant reactions.<sup>1</sup>

The applications of polyoxometalates are based on their unique properties, including size, electron- and proton-transfer/storage abilities, thermal stability, lability of the lattice oxygen, and high Brønsted acidity of the corresponding acids.<sup>2</sup>

In medicinal chemistry, polyoxometalates exhibit biological activity, such as highly selective inhibition of enzymes and in vitro and in vivo antitumoral, antiviral, and antiretroviral activities.<sup>3</sup>

Polyoxometalate compounds provide a good basis for the molecular design of mixed oxide catalysts, and they have high

capability in practical uses. The catalytic function of polyoxometalate compounds is used in solution as well as in the solid state, as acid<sup>4</sup> and reduction<sup>5,6</sup> catalysts. The research activity in the field of polyoxometalates is very high and still growing.

Since the first report by Finke and Droege in 1983,<sup>7</sup> the synthesis of sandwich polyoxometalates derived from the trivalent anion  $\alpha$ -[P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>]<sup>12-</sup> (abbreviated as P<sub>2</sub>W<sub>15</sub>) has received increased attention because of their physicochemical and catalytic properties.<sup>4–6</sup> These compounds result from the reaction of the trivalent anion  $\alpha$ -[P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>]<sup>12-</sup> with transition-metal cations (M = Mn<sup>II</sup>, Fe<sup>III</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup>, and Cd<sup>II</sup>).

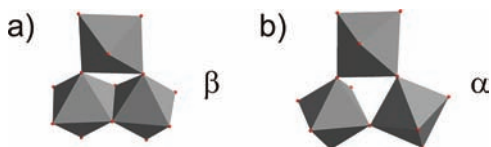
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When a sheet of four M atoms is sandwiched between two  $\{P_2W_{15}\}$  subunits, complexes of the formula  $[M_4(H_2O)_2(P_2W_{15}O_{56})_2]^{n-}$  are obtained.<sup>8</sup> Such complexes can be considered as “saturated” because they possess the maximum number of d metal centers that can be sandwiched by two trivacant anions  $\{P_2W_{15}\}$ .

For all known Dawson tetranuclear sandwich complexes characterized by X-ray diffraction, the “classical”  $\beta\beta$  configuration is observed with  $\beta$  connectivities between both trivacant  $\{P_2W_{15}\}$  units and the central  $M_4$  tetrad (Scheme 1a).<sup>8b,d,e,g,k</sup>

Scheme 1. Representations of the (a)  $\beta$  and (b)  $\alpha$  Junctions



Let us remind the reader that the  $\beta$  junction implies a connection between one  $WO_6$  and a dimetallic unit  $W_2O_{10}$ , whereas the  $\alpha$  junction is defined as a bis( $\mu$ -oxo) connection between two dimeric units  $W_2O_{10}$  (Scheme 1); alternately, the  $\alpha$  junction may be described by a group of three mutually corner-coupled  $WO_6$  octahedra.<sup>9</sup>

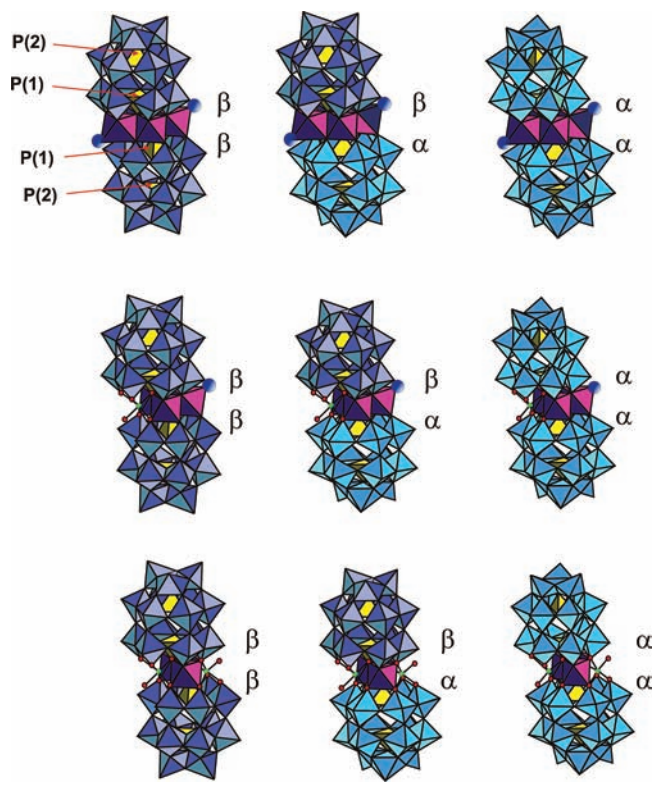
Nevertheless, in the case of the tetracobalt sandwich complexes, we have reported that in neutral medium a mixture of  $\beta\beta$  and  $\alpha\beta$  configurations has been observed.<sup>19</sup>

Dinuclear and trinuclear sandwich complexes  $[(NaOH)_2M_2(P_2W_{15}O_{56})_2]^{n-}$  and  $[(NaOH)_3M_3(H_2O)(P_2W_{15}O_{56})_2]^{n-}$  ( $M = Co^{II}, Mn^{II}, Ni^{II}$ , and  $Fe^{III}$ )<sup>10–14</sup> were also obtained (Scheme 2). The first example of a sandwich-type species with less than four d metals was reported by Hill et al.<sup>12</sup> X-ray structures of the di- and triiron derivatives as well as of the trimanganese and tricobalt derivatives have been reported.<sup>11–13</sup> For the diiron sandwich  $[(NaOH)_2Fe_2(P_2W_{15}O_{56})_2]^{16-}$  [symbolized as  $Na_2Fe_2(P_2W_{15})_2$ ], the junctions between the trivacant units  $\{P_2W_{15}\}$  and the metallic sheet are both of  $\alpha$  type (Scheme 2), whereas in the case of the triiron complex, the structure may be considered as resulting from the fusion of one  $\alpha$ - $\{Fe_3(P_2W_{15})\}$  unit and one “lacunary”  $\beta$ - $\{NaFe_2(P_2W_{15})\}$  unit, where the central sheet consists of three d metals and one labile  $Na^+$  cation.

A similar  $\alpha\beta$  connectivity has been reported for tricobalt species  $[(NaOH)_2Co_3(H_2O)(P_2W_{15}O_{56})_2]^{17-}$  [abbreviated as  $NaCo_3(P_2W_{15})_2$ ; Scheme 2];<sup>10,11</sup> in contrast, the trimanganese derivative exhibits a  $\beta\beta$  connectivity for both trivacant moieties  $\{P_2W_{15}\}$ .<sup>13</sup> This suggests that the nature and number of transition-metal cations in the central sheet as well as the conditions of the synthesis play an important role for the type of connectivity.<sup>15</sup> Moreover, the pH, the ratio of transition-metal cation to trivacant moieties  $\{P_2W_{15}\}$ , the concentration, and the ionic strength also play crucial roles in the preparation of pure compounds.

Because the  $Na^+$  cations are weakly bonded and labile,  $[(NaOH)_2M_2(P_2W_{15}O_{56})_2]^{n-}$  and  $[(NaOH)_3M_3(H_2O)(P_2W_{15}O_{56})_2]^{n-}$  complexes may act as a divacant and monovacant lacunary species, respectively. Thus, mixed-metal sandwich complexes can be obtained easily by the reaction of a transition-metal cation  $M^{n+}$  with  $Na_2Fe_2(P_2W_{15})_2$ . Indeed, it was shown that  $\alpha\alpha$ - $Na_2Fe_2(P_2W_{15})_2$  reacts with  $M^{2+}$  ( $M = Mn, Co, Ni, Zn$ ), leading to a “saturated” mixed-metal sandwich-

Scheme 2. Structural Relationship between the Different Cobalt Sandwich Complex Isomers Based on  $\alpha$ - $[P_2W_{15}O_{56}]^{12-}$ :  $Co_4(P_2W_{15})_2$  (Top);  $NaCo_3(P_2W_{15})_2$  (Center);  $Na_2Co_2(P_2W_{15})_2$  (Bottom)



type polyanion  $[M^{II}_2(H_2O)_2Fe^{III}_2(P_2W_{15}O_{56})_2]^{14-}$  [abbreviated as  $M_2Fe_2(P_2W_{15})_2$ ].<sup>12,16,17</sup> Two  $M^{2+}$  replace the two  $Na^+$  ions of  $Na_2Fe_2(P_2W_{15})_2$  with the simultaneous rearrangement of the whole structure back to the conventional inter-POM-unit connectivity  $\beta\beta$  junction. At relatively high pH (ca. 5–6),  $\alpha\alpha$ - $Na_2Fe_2(P_2W_{15})_2$  incorporates only one transition-metal cation  $M$  ( $M = Fe^{3+}, Co^{2+}, Cu^{2+}$ ) into the central sheet to yield a still “lacunary” sandwich species, with one  $\alpha$  junction and one  $\beta$  junction between the trivacant  $\{P_2W_{15}\}$  subunits and the  $\{NaMFe_2\}$  unit.<sup>12b</sup>

Similarly, the “lacunary” sandwich complex  $\alpha\beta$ - $NaCo_3(P_2W_{15})_2$  can add one  $Co^{2+}$  cation to form nearly quantitatively an unsymmetrical tetracobalt sandwich complex  $\alpha\beta$ - $[Co_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$  [symbolized as  $\alpha\beta$ - $Co_4(P_2W_{15})_2$ ].<sup>18</sup> This synthesis proceeds at pH around 6.5 and high reactant concentrations; using different conditions leads to a mixture of various complexes.

Herein we report the study of the interconversion between  $\alpha\beta$ - $Co_4(P_2W_{15})_2$  and  $\beta\beta$ - $Co_4(P_2W_{15})_2$  as well as the decomplexation process at low pH, leading to the formation of  $\alpha\beta$ - $NaCo_3(P_2W_{15})_2$  and  $\alpha\beta$ - $Na_2Co_2(P_2W_{15})_2$ . This system was investigated under various conditions (pH and concentration) by electrochemistry, UV–visible absorption spectroscopy, and <sup>31</sup>P NMR spectroscopy.

## RESULTS AND DISCUSSION

**Preliminary Considerations.** All syntheses were performed starting from  $\alpha$ - $[P_2W_{15}O_{56}]^{12-}$  prepared from pure  $\alpha$ - $[P_2W_{18}O_{62}]^{6-}$ .

We previously reported the synthesis of the  $\text{Co}_4(\text{P}_2\text{W}_{15})_2$  species from  $\text{Co}^{2+}$  and  $\alpha\text{-}[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ .<sup>19</sup> The  $^{31}\text{P}$  NMR spectrum of the compound obtained via synthesis in a neutral medium indicated the presence of a mixture of the symmetrical  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  ( $\delta = +1459$  and  $+9.8$  ppm) and unsymmetrical  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  ( $\delta = +1551, +1242, +16.7,$  and  $+12.3$  ppm) complexes in relative proportions 38 and 62% (by integration of the NMR resonances).<sup>19,20</sup> Unfortunately, the solubilities of these two compounds are very close, which precludes their separation by selective precipitation or crystallization. Thus, a neutral medium is not an optimal condition for the synthesis of  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ .

On the contrary, optimal conditions for the synthesis of the symmetrical  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ , from  $\text{Co}^{2+}$  and  $\alpha\text{-}[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ , required an acidic medium (pH  $\sim 3$ ).<sup>19</sup> Indeed, in contrast to a neutral medium, synthesis in an acidic solution (pH  $\approx 3$ ) gives exclusively the symmetrical  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  species with a purity of 95%.

Concerning the unsymmetrical species  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ , the best method of synthesis consists of starting from the sandwich complex  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$ .<sup>18</sup> This synthesis requires a neutral medium, i.e., pH 6.5. The formation of the "saturated" tetracobalt species  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  was followed by  $^{31}\text{P}$  NMR in solution. The  $^{31}\text{P}$  NMR solution spectrum of the starting compound  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$  presents two narrow lines [ $\Delta\nu_{1/2} = 10$  Hz, P(2) farthest from the tricobalt central cluster] of equal intensity, at  $\delta = -9.3$  and  $+22.0$  ppm, and two broad bands ( $\Delta\nu_{1/2} = 450$  Hz) at  $\delta = +1125$  and  $+1673$  ppm [P(1) nuclei close to the tricobalt central cluster; see Table 1].

**Table 1.**  $^{31}\text{P}$  NMR Data for the Cobalt Sandwich Species Obtained from Pure Compounds<sup>a</sup>

compound	P(1) <sup>b</sup>		P(2) <sup>b</sup>	
	$\delta^c$	$\Delta\nu_{1/2}^d$	$\delta^c$	$\Delta\nu_{1/2}^d$
$\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$	+1483	420	+9.9	20
$\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$	+1203	420	+10.0	20
	+1522	420	+14.5	20
$\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$	+1125	450	-9.3	10
	+1673	450	+22.0	10
$\text{Na}_2\text{Co}_2(\text{P}_2\text{W}_{15})_2$	+1299	300	+4.2	10

<sup>a</sup>0.02 mol L<sup>-1</sup> unbuffered solution in D<sub>2</sub>O/H<sub>2</sub>O (1:1) measured at 300 K. <sup>b</sup>P(1) and P(2) in the PW<sub>6</sub> and PW<sub>9</sub> subunits, respectively. <sup>c</sup>In ppm with respect to 85% H<sub>3</sub>PO<sub>4</sub>. <sup>d</sup>In Hz.

The addition of  $\text{Co}^{2+}$  to the aqueous solution of  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$  (pH 6.5) induces the appearance of new signals in the  $^{31}\text{P}$  NMR spectrum, namely, two narrow lines ( $\Delta\nu_{1/2} = 20$  Hz) at  $\delta = +10.0$  and  $+14.5$  ppm [P(2)] and two broad bands ( $\Delta\nu_{1/2} = 420$  Hz) at  $\delta = +1203$  and  $+1522$  ppm [P(1); see Table 1], corresponding to the saturated tetracobalt species  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ .

A total of 1 equiv of  $\text{Co}^{2+}$  per  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$  should be sufficient to convert it quantitatively to  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ . However, for synthetic purposes, in order to obtain the highest yield of  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ , we have processed with a 2-fold excess (2 equiv) of  $\text{Co}^{2+}$  with respect to the reaction stoichiometry.

**Study of the  $\alpha\beta\text{-}\beta\beta$  Interconversion for  $\text{Co}_4(\text{P}_2\text{W}_{15})_2$  complex.** After the addition of 2 equiv of  $\text{H}_3\text{O}^+$  (pH ca. 1.70), to the unbuffered solution containing the dissymmetrical  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  ( $c = 0.02$  mol L<sup>-1</sup>), it evolves slowly into its

symmetrical  $\beta\beta$  isomer. The pH of the solution evolves also slightly, with a final pH around 2.5.

A preliminary study of the reaction was conducted by  $^{31}\text{P}$  NMR spectroscopy: the region of P(2) shows the vanishing of signals at  $+14.5$  and  $+10.0$  ppm<sup>18,19</sup> attributed to the dissymmetrical complex  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  and the formation of one transient species, which has been identified as  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$ <sup>10,11</sup> (black circle symbols in Figure 1b).

Analysis of these data implies the following successive reactions: (i) decomplexation of the dissymmetrical  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  compound to form the monolacunary  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$ , (ii) isomerization of  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$  by the formal rotation of a whole  $\alpha\text{-P}_2\text{W}_{15}$  subunit, leading to both  $\beta\text{-type}$  junctions at the  $\text{NaCo}_3$  tetrad, and finally (iii) recomplexation with  $\text{Co}^{2+}$  (dotted square part, Scheme 3).

The second step, which implies a structural rearrangement, is likely a slow process, whereas recomplexation of  $\text{Co}^{2+}$  is likely relatively rapid. These may explain why the concentration of  $\beta\beta\text{-NaCo}_3\text{P}_4\text{W}_{30}$  remains too low to be observed by  $^{31}\text{P}$  NMR spectroscopy.

Additional experiments show that the reaction is complete only with 2 equiv of  $\text{H}_3\text{O}^+$  per sandwich complex; thus, pure  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  is obtained after 90 min (Figure 1c).

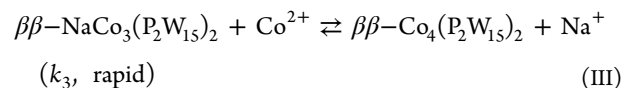
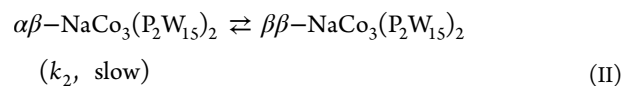
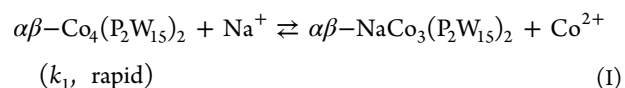
In order to follow more easily the interconversion process, the study was performed in a buffered solution at higher pH (pH 3.0). Indeed, the pH increase leads to a slowdown of the kinetics of the reactions.

The detailed study was conducted by  $^{31}\text{P}$  NMR spectroscopy using  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  ( $c = 0.02$  mol L<sup>-1</sup>) in D<sub>2</sub>O/H<sub>2</sub>O (1:1) in 0.5 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> at pH 3.0 (Figure 2).

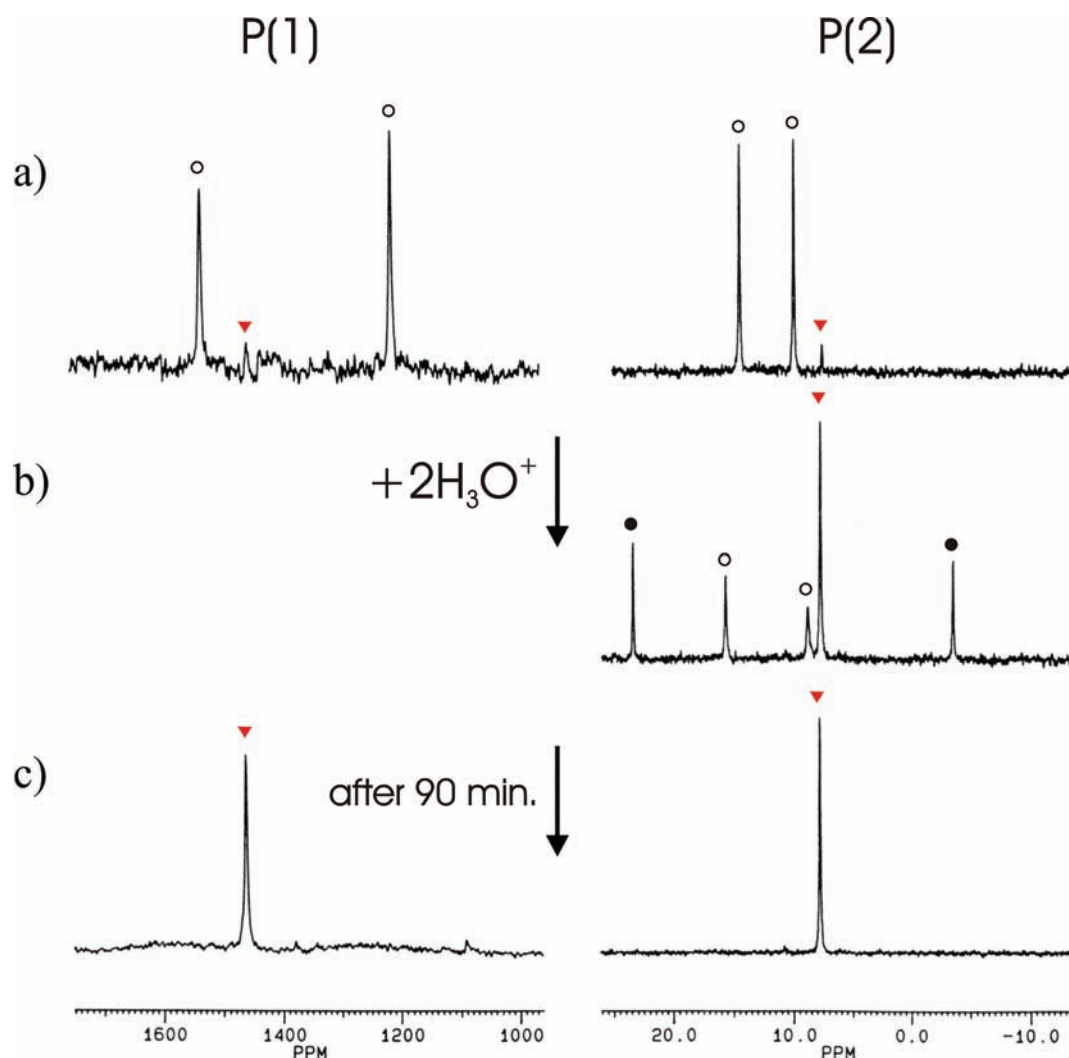
The  $^{31}\text{P}$  NMR spectra were recorded only in the low-frequency region (from  $-15$  to  $+25$  ppm), i.e., for P(2) nuclei far from the paramagnetic centers. The relative concentrations of the different species are obtained by integration of the  $^{31}\text{P}$  NMR signals.

It should be noticed that, immediately (i.e. ca. 3 min) after preparation of the solution, already 46% of  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  disappeared, leading to unsaturated  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$  ( $+22.4$  and  $-7.5$  ppm) and saturated  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  (ca. 38% and 8%, respectively). The concentrations of  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  and  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$  decrease with time for the benefit of the symmetrical complex  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  (signal at  $+7.6$  ppm).<sup>19,20</sup>

In accordance with the assumption proposed before, the present results may also be analyzed as follows:



The first step leading to the formation of  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$  is very fast. The second step implies important structural rearrangements, which is consistent with the slowness of this process, whereas complexation of transient species with  $\text{Co}^{2+}$  remains always relatively rapid. Isomer  $\beta\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$  is still not observed, which suggests that the last equilibrium proceeds without a significant concentration of the inter-



**Figure 1.** 121.5 MHz  $^{31}\text{P}$  NMR study (a) of  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  as the initial spectrum, (b) immediately after the addition of 2 equiv of  $\text{H}_3\text{O}^+$  [the P(1) region is not given because the acquisition needs several minutes to be achieved], and (c) after 90 min with  $c = 2 \times 10^{-2} \text{ mol L}^{-1}$  in  $\text{D}_2\text{O}/\text{H}_2\text{O}$  (1:1) and pH ca. 1.7: ( $\blacktriangledown$ ) symmetrical  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ ; ( $\circ$ ) unsymmetrical  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ ; ( $\bullet$ )  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$ . Left part: region of the P(1) atoms. Experimental conditions: spectral width 125 kHz; pulse width 2  $\mu\text{s}$  (ca.  $40^\circ$  flip angle); 8K data points; acquisition time 33 ms; ca. 10000 transients acquired without relaxation delay; line broadening factor 40 Hz. Right part: region of the P(2) atoms. Experimental conditions: spectral width 9 kHz; pulse width 2  $\mu\text{s}$  (ca.  $40^\circ$  flip angle); 4K data points; acquisition time 0.23 s; ca. 1000 transients acquired without relaxation delay; line broadening factor 4 Hz.

mediate species and, consequently, that reaction (III) is more rapid than reaction (II) ( $k_3 \gg k_2$ ).

**Effect of the pH on the  $\alpha\beta$ - $\beta\beta$  Interconversion.** We have already shown by  $^{31}\text{P}$  NMR (Figure 3), electrochemistry, and UV-visible absorption spectroscopy that, at pH >3.5 and in high concentration ( $\geq 2 \times 10^{-2} \text{ mol L}^{-1}$ ),  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ ,  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ , and  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$  are stable for at least 1 month.<sup>10,18</sup> Only in the case of  $\text{Na}_2\text{Co}_2(\text{P}_2\text{W}_{15})_2$  an isomerization has been observed.<sup>10</sup>

We have also shown earlier that, at the same concentration ( $2 \times 10^{-2} \text{ mol L}^{-1}$ ) but at lower pH ( $2.5 < \text{pH} < 3.5$ ),  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  isomerizes to  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  through formation of the transient  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$  species (Figure 4A).

Finally, in a more acidic solution (pH 2.0 and concentration always the same, i.e.,  $2 \times 10^{-2} \text{ mol L}^{-1}$ ), the sandwich complexes  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  dissociate. Indeed, this dissociation has been detected by electron paramagnetic resonance spectroscopy where eviction of  $\text{Co}^{2+}$  has been observed.<sup>21</sup> This result seems to contradict the preliminary study of  $\alpha\beta$ - $\beta\beta$

interconversion for the  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  complex obtained after the addition of 2 equiv of  $\text{H}_3\text{O}^+$  to the solution containing  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ . However, this experiment was conducted in an unbuffered solution, where the pH of the solution is increased during this process, with a final pH around 2.5, a pH where the symmetrical  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  complex is stable.

Moreover, a different  $^{31}\text{P}$  NMR final spectrum [P(2) region; Figure 4B] is obtained. In that case, the evolution is also very fast and the final state is already reached before the end of the first  $^{31}\text{P}$  NMR recording. It contains a series of four low-intensity signals between 0 and 4 ppm, which might be attributed to the different isomers of  $\text{Na}_2\text{Co}_2(\text{P}_2\text{W}_{15})_2$ . In addition, five more intense  $^{31}\text{P}$  NMR signals are observed between  $-5.0$  and  $+23.0$  ppm: (i) the major peak at 7.8 ppm is assigned to the compound  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ , (ii) the first pair of signals, at  $-4.9$  and  $+23.0$  ppm, corresponds to  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$  (see Table 1),<sup>10</sup> and (iii) the second pair, at  $-2.0$  and  $+16.5$  ppm, should be attributed to a new dissymmetrical compound  $\beta\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$  [indeed  $\alpha\beta$ -

Scheme 3. Proposed Equilibrium between  $\beta\beta$ - and  $\alpha\beta$ - $\text{Co}_4(\text{P}_2\text{W}_{15})_2$ ,  $\beta\beta$ - and  $\alpha\beta$ - $\text{NaCo}_3(\text{P}_2\text{W}_{15})_2$  and Isomers of  $\text{Na}_2\text{Co}_2(\text{P}_2\text{W}_{15})_2$

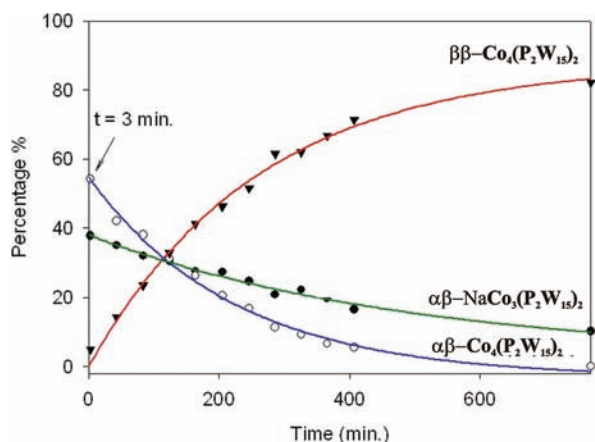
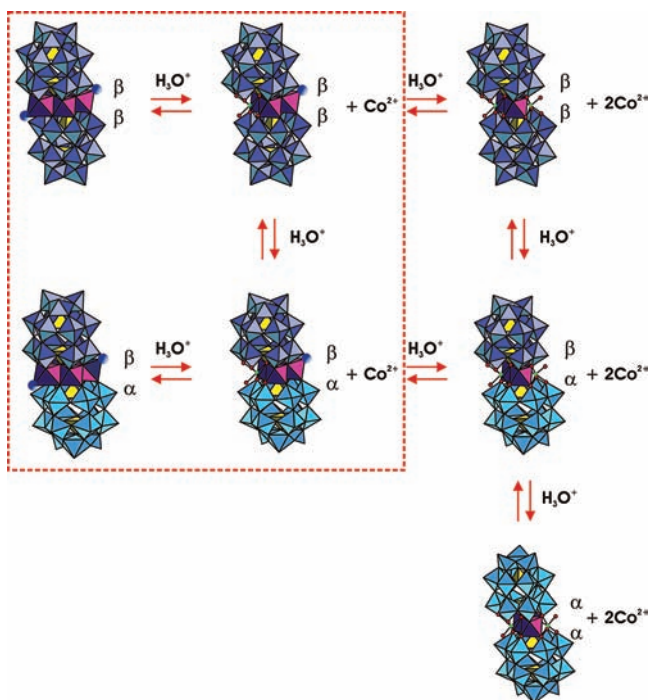


Figure 2. Kinetic study at the low-frequency part [P(2) region] of the 121.5 MHz  $^{31}\text{P}$  NMR spectra of the formation of  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  from  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  in  $\text{D}_2\text{O}/\text{H}_2\text{O}$  (1:1) in  $0.5 \text{ mol L}^{-1} \text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$  (pH 3.0).  $c = 2 \times 10^{-2} \text{ mol L}^{-1}$ .  $T = 300 \text{ K}$ . Plot of the percentage of  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ ,  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ , and  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$  versus time (min). The symbols  $\blacktriangledown$  indicate signals belonging to  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ ,  $\bullet$  correspond to  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$ , and  $\circ$  to  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ .

$\text{Co}_4(\text{P}_2\text{W}_{15})_2$  seems absent because two peaks at +10.0 and +14.5 ppm should be present in this case; see Table 1]. Thus, these signals might be assigned to the monolacunary species  $\beta\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$  (see Scheme 3).

For  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ , evolution toward a similar distribution of saturated mono- and bilacunary species is also observed.

**Effect of the Concentration on the  $\alpha\beta$ - $\beta\beta$  Interconversion.** However, a different behavior is observed for  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  in a diluted solution ( $5 \times 10^{-4} \text{ mol L}^{-1}$ ) and also at relatively low pH (pH <3.5; Figure 4C). In such a diluted

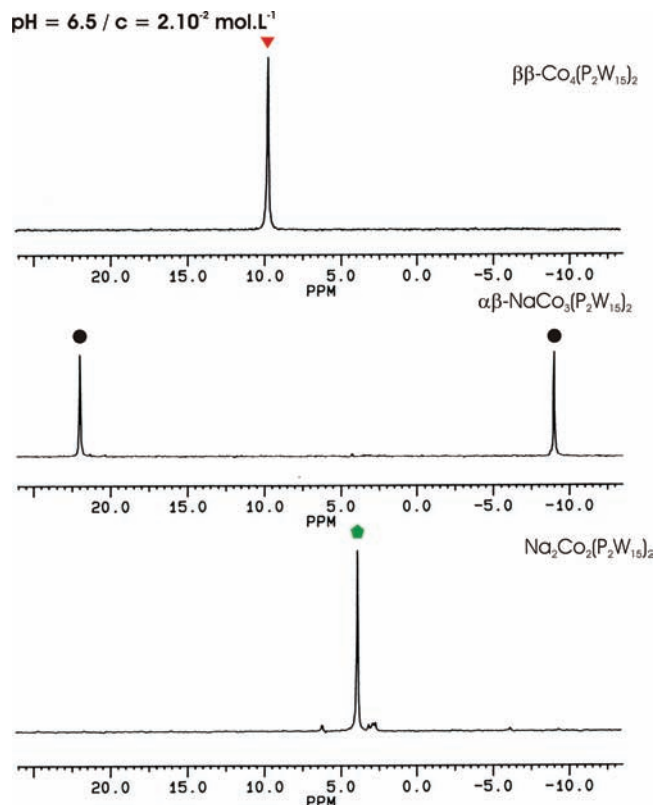


Figure 3. Low-frequency part [P(2) region] 121.5 MHz  $^{31}\text{P}$  NMR spectra of  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ ,  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$ , and  $\text{Na}_2\text{Co}_2(\text{P}_2\text{W}_{15})_2$  (at  $t = 0$ );  $c = 2 \times 10^{-2} \text{ mol L}^{-1}$  of  $0.5 \text{ mol L}^{-1} \text{Na}_2\text{SO}_4$  (pH 6.5)/ $\text{D}_2\text{O}$  (2:1).  $T = 300 \text{ K}$ .

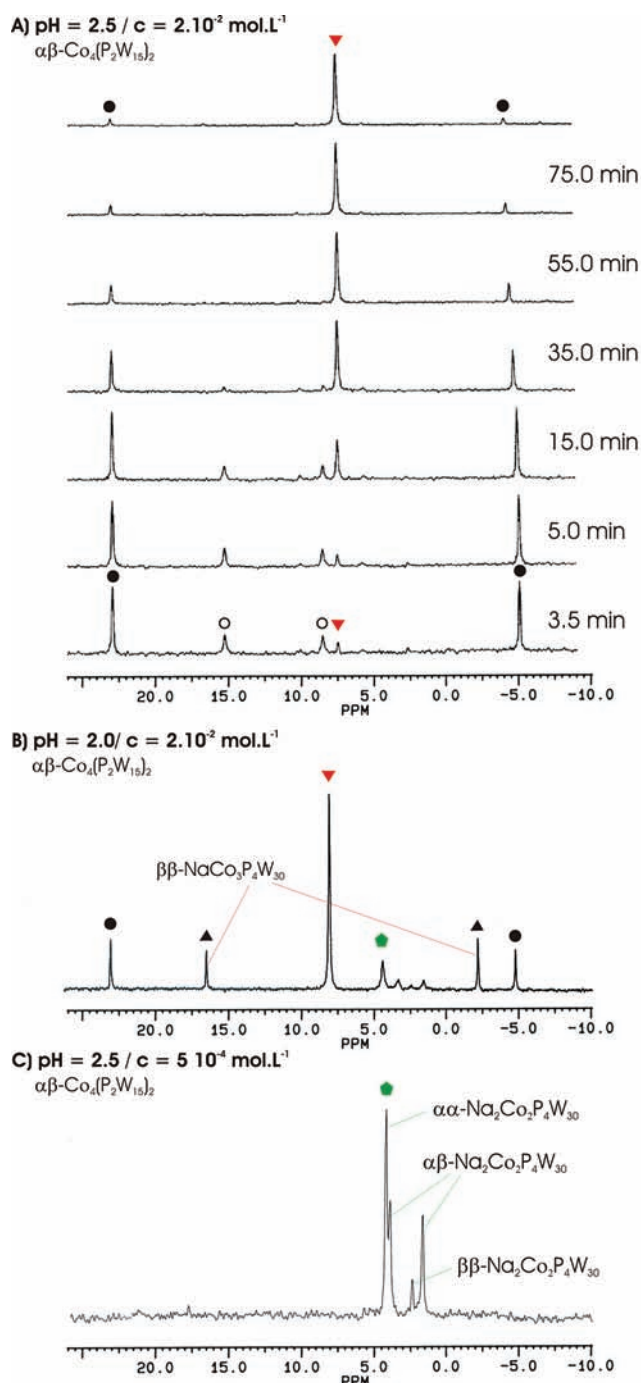
solution, new species are identified, but neither the saturated symmetric  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  nor the unsaturated  $\text{NaCo}_3(\text{P}_2\text{W}_{15})_2$  is observed.

The kinetics of the evolution is very fast because the reaction is already completed before the end of acquisition of the first  $^{31}\text{P}$  NMR spectrum (ca. 5 min). It consists [P(2) region] of a series of four peaks between 0 and 4 ppm (Figure 4C).

In similar experimental conditions (pH and concentration), the same spectrum is obtained, whatever the nature of the starting cobalt sandwich complex, i.e.,  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ ,  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$ , and  $\alpha\alpha\text{-Na}_2\text{Co}_2(\text{P}_2\text{W}_{15})_2$ .<sup>10</sup>

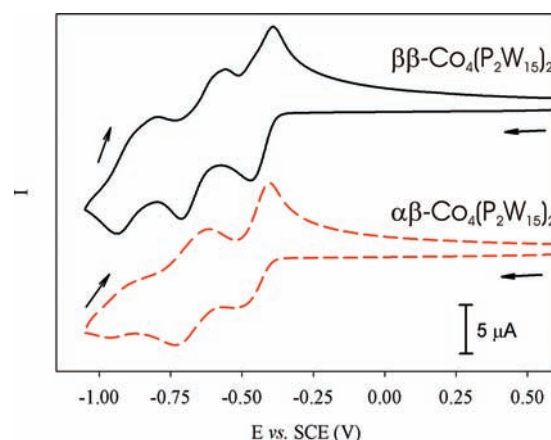
According to the very narrow range of P(2) chemical shifts, the four signals likely belong to dinuclear cobalt sandwich complexes obtained after the eviction of one [from  $\text{NaCo}_3(\text{P}_2\text{W}_{15})_2$ ] or two [from  $\text{Co}_4(\text{P}_2\text{W}_{15})_2$ ] external Co atoms. These peaks may be attributed to the mixture of  $\alpha\alpha$ ,  $\beta\beta$ , and  $\alpha\beta$  isomers of  $\text{Na}_2\text{Co}_2(\text{P}_2\text{W}_{15})_2$ , where the two first isomers ( $\alpha\alpha$  and  $\beta\beta$ ) are symmetrical (one signal each), whereas the last one ( $\alpha\beta$ ) is dissymmetrical and should present two signals.

According to these results, in a diluted solution and an acidic medium (pH <3.5),  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  likely evolves to a monolacunary species  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$  by eviction of an external Co atom; this first step is followed immediately by the departure of the second external Co atom. The resulting bilacunary species  $\alpha\beta\text{-Na}_2\text{Co}_2(\text{P}_2\text{W}_{15})_2$  then isomerizes partially to  $\alpha\alpha\text{-Na}_2\text{Co}_2(\text{P}_2\text{W}_{15})_2$  and  $\beta\beta\text{-Na}_2\text{Co}_2(\text{P}_2\text{W}_{15})_2$ . The three isomers stay in equilibrium (Scheme 3). In the case of  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ , the first step should lead to  $\beta\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$ , which evolves similarly to the same mixture of  $\text{Na}_2\text{Co}_2(\text{P}_2\text{W}_{15})_2$  through both  $\beta\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$  and/or  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$ .



**Figure 4.** Low-frequency [part P(2) region] 121.5 MHz <sup>31</sup>P NMR spectra of  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ .  $T = 300$  K. Evolution at (A) pH 2.5 and  $c = 2 \times 10^{-2}$  mol L<sup>-1</sup>, (B) pH 2.0 and  $c = 2 \times 10^{-2}$  mol L<sup>-1</sup>, and (C) pH 2.5 and ( $c = 5 \times 10^{-4}$  mol L<sup>-1</sup>).

Thus, both the concentration of the polyoxometalate and the pH of the solution are crucial parameters for the stability and interconversion of cobalt sandwich compounds. All of the results suggest that, at pH < 3.5, tetracobalt species first lose one external Co atom to form a monolacunary complex  $\text{NaCo}_3(\text{P}_2\text{W}_{15})_2$ . Second, depending on the concentration, the monolacunary complex  $\text{NaCo}_3(\text{P}_2\text{W}_{15})_2$  can be isomerized and react with  $\text{Co}^{2+}$  to give back the saturated complex ( $\alpha\beta$ – $\beta\beta$  interconversion) or could lose a second Co atom to form the bilacunary species  $\text{Na}_2\text{Co}_2(\text{P}_2\text{W}_{15})_2$  (Scheme 3).



**Figure 5.** Cyclic voltammograms of  $5 \times 10^{-4}$  mol L<sup>-1</sup>  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  and  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  in  $0.5$  mol L<sup>-1</sup>  $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$  (pH 3.5). Scan rate:  $20$  mV s<sup>-1</sup>.

**Kinetic Study Followed by Electrochemistry.** We have already shown that both  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  and  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  are stable in an aqueous solution in the range  $3.5 \leq \text{pH} \leq 7.5$  whatever the concentration ( $\geq 0.5$  mmol L<sup>-1</sup>).<sup>17</sup> At these concentrations, symmetrical  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  presents three processes of reduction between  $-0.30$  and  $-0.95$  V versus saturated calomel electrode (SCE) corresponding to the reduction of W ( $\text{W}^{\text{VI}}/\text{W}^{\text{V}}$ ). These three processes are reversible and involve four electrons each. The third wave is split by 85 mV (Table 2); this splitting is more easily detected in differential pulse voltammetry (DPV). In the case of the dissymmetrical  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ , we still observe three processes of reduction, but the waves are broader (Figure 5).

However, a different behavior is observed at pH < 3.5, where interconversion and decomplexation processes are observed. While in the case of  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  evolution is relatively slow, for  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ , the first state is already reached during the preparation of the solution.

Figure 6 presents the evolution with time of the cyclic voltammetry (CV) and DPV of  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  in an aqueous solution (pH 2.5 and  $c = 5 \times 10^{-4}$  mol L<sup>-1</sup>). In the initial state,  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  presents also three processes of reduction between  $-0.30$  and  $-0.95$  V corresponding to the reduction of W ( $\text{W}^{\text{VI}}/\text{W}^{\text{V}}$ ). These three processes are still reversible and also involve four electrons per process, and the third wave is again split, by ca 50 mV (Table 2).

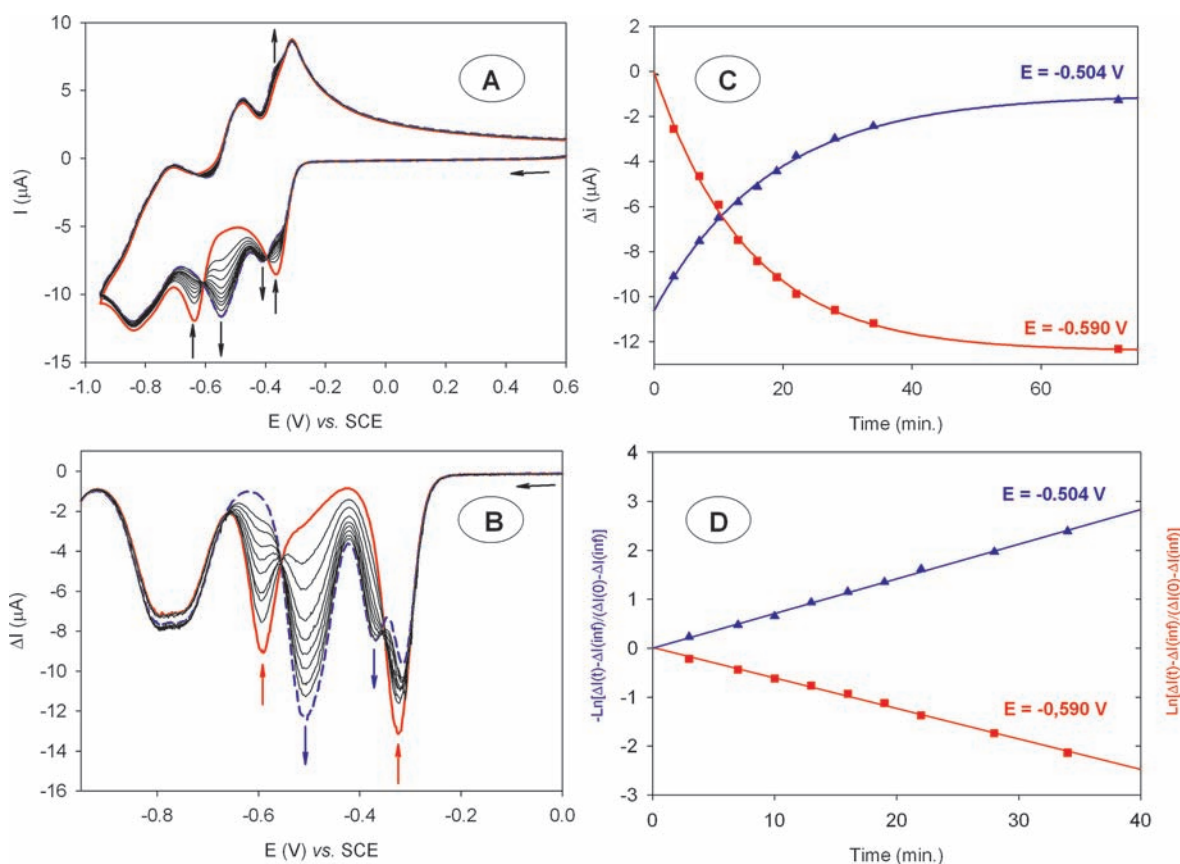
The change with time (in the range 0–60 min) of the CV curves at pH 2.5 and  $c = 5 \times 10^{-4}$  mol L<sup>-1</sup> shows the presence of several “isovoltamperometric” points (analogue to isosbestic points in UV–visible absorption spectroscopy). These results suggest evolution of the initial compound to the final ones without significant concentration of any transient species. During evolution, the first reduction process is split into two bielectronic reversible waves. At the level of the second reduction process, we also note the vanishing of the initial wave of reduction at  $-0.636$  V for the benefit of a new wave at  $-0.544$  V. Finally, we do not notice any change for the third process of reduction (Figure 6A).

Evolution with time of the DPV curves in the same conditions of concentrations and pH shows again the presence of two isovoltamperometric points. At the level of the second reduction process, we observe the progressive decrease of a peak at  $-0.504$  V and the increase of a new peak at  $-0.590$  V. The corresponding kinetic data are represented in Figure 6C,D:

Table 2. Electrochemical Data at pH 3.5 and 2.5 of the Tetra-, Tri-, and Dinuclear Dawson-Derived Sandwich Complexes<sup>a</sup>

compound	pH 2.5			pH 3.5		
	W(1)	W(2)	W(3)	W(1)	W(2)	W(3)
$\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$	-0.365 (4e, 53)	-0.556 (4e, 160)	-0.785 (2e, 72)	-0.436 (4e, 71)	-0.641 (4e, 144)	-0.832 (2e, 64)
	-0.354 (2e, 60)	-0.534 (4e, 80)	-0.835 (2e, 91)			-0.917 (2e, 94)
	-0.416 (2e, 66)		-0.788 (2e, 74)			
$\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$	-0.349 (2e, 47) <sup>b</sup>	-0.532 (4e, 76) <sup>b</sup>	-0.760 (2e, 89) <sup>b</sup>	-0.467 (4e, 126)	-0.673 (4e, 114)	-0.903 (4e, 100)
	-0.406 (2e, 61) <sup>b</sup>		-0.831 (2e, 73) <sup>b</sup>			
$\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$	-0.357 (2e, 54) <sup>b</sup>	-0.537 (4e, 82) <sup>b</sup>	-0.761 (2e, 82) <sup>b</sup>	-0.470 (2e, 93)	-0.660 (4e, 83)	-0.835 (4e, 65)
	-0.413 (2e, 54) <sup>b</sup>		-0.838 (2e, 67) <sup>b</sup>	-0.531 (2e, 58)		
$\text{Na}_2\text{Co}_2(\text{P}_2\text{W}_{15})_2$	-0.348 (2e, 44) <sup>b</sup>	-0.529 (4e, 81) <sup>b</sup>	-0.759 (2e, 94) <sup>b</sup>			
	-0.408 (2e, 56) <sup>b</sup>		-0.833 (2e, 71) <sup>b</sup>			

<sup>a</sup>All redox potentials  $E^\circ$ , approximated by  $(E_p^a + E_p^c)/2$  for the reversible steps, are given in V versus SCE as obtained from cyclic voltammetry ( $\nu = 20 \text{ mV s}^{-1}$ ) in  $0.5 \text{ M Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$  (pH 2.5). Glassy carbon electrode. Under bracket: (number of electrons  $n$ ; peak splitting  $\Delta E_p$ ).  $\Delta E_p$  is the difference potential between the oxidative and reductive peak potentials. <sup>b</sup>The potentials correspond to the evolved solution, where the kinetic of evolution is too rapid at pH < 3.5 for  $\alpha\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ ,  $\alpha\beta\text{-NaCo}_3(\text{P}_2\text{W}_{15})_2$ , and  $\text{Na}_2\text{Co}_2(\text{P}_2\text{W}_{15})_2$ . <sup>c</sup>  $c = 5 \times 10^{-4} \text{ mol L}^{-1}$ .



**Figure 6.** Evolution with time of (A) the CV (scan rate  $20 \text{ mV s}^{-1}$ ) and (B) the DPV (scan rate  $25 \text{ mV s}^{-1}$ ) of  $5 \times 10^{-4} \text{ mol L}^{-1} \beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$  in  $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$  (pH 2.5). Glassy carbon electrode  $\phi = 3 \text{ mm}$ . (C) Plot of the cathodic peak current  $\Delta i_{pc}$  measured at  $-0.504$  and  $-0.590 \text{ V}$  versus SCE and obtained from the DPV mode versus time (min). (D) Plots of  $+\ln\{[\Delta i(t) - \Delta i(\infty)]/[\Delta i(0) - \Delta i(\infty)]\}$  (red line) and of  $-\ln\{[\Delta i(t) - \Delta i(\infty)]/[\Delta i(0) - \Delta i(\infty)]\}$  (blue line) versus time (min).  $\Delta i_{pc}$  measured respectively at  $-0.590$  and  $-0.504 \text{ V}$  versus SCE and obtained from the DPV mode versus time (min). For more clarity, because similar slopes are observed at  $-0.590$  and  $-0.504 \text{ V}$  versus SCE,  $-\ln\{[\Delta i(t) - \Delta i(\infty)]/[\Delta i(0) - \Delta i(\infty)]\}$  versus time (min) is plotted for  $-0.504 \text{ V}$  (blue line).

the peak currents  $\Delta i$  measured at  $-0.504$  and  $-0.590 \text{ V}$  are plotted versus time. We observe simultaneously an exponential decrease of  $\Delta i$  measured at  $-0.504 \text{ V}$  as well as an exponential growth of  $\Delta i$  measured at  $-0.590 \text{ V}$ . The plot of  $\pm \ln\{[\Delta i(t) - \Delta i(\infty)]/[\Delta i(0) - \Delta i(\infty)]\}$  versus time agrees with a pseudo-first-order reaction for both potentials (Figure 6D).

From these plots, the apparent kinetic constant may be easily obtained, namely,  $k_{app}^+ = 0.071 \pm 0.009 \text{ min}^{-1}$  (at  $-0.504 \text{ V}$ )

and  $k_{app}^- = 0.062 \pm 0.009 \text{ min}^{-1}$  (at  $-0.590 \text{ V}$ ). Lowering the pH leads to the reaction proceeding faster (Table 3).

#### Kinetic Study Followed by UV–Visible Spectroscopy.

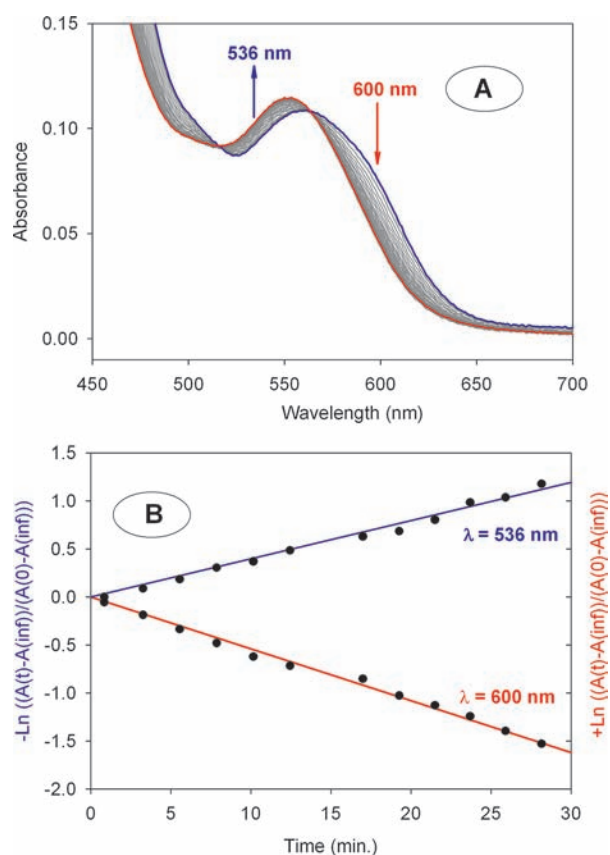
To confirm these results, a kinetic study in the same conditions (i.e., concentration and pH) was conducted by UV–visible spectroscopy also from  $\beta\beta\text{-Co}_4(\text{P}_2\text{W}_{15})_2$ .

**Table 3.** Pseudo-First-Order Kinetic Constants for Evolution of  $\beta\beta$ - $\text{Co}_4(\text{P}_2\text{W}_{15})_2$  Determined from the Electrochemical and UV–Visible Data

pH	$[\text{H}_3\text{O}^+]/[\text{POM}]^a$	$k_{\text{app}}^-$ ( $\text{min}^{-1}$ )		$k_{\text{app}}^+$ ( $\text{min}^{-1}$ )	
		UV–visible	electrochemistry	UV–visible	electrochemistry
3.50	0.6				
3.00	2.0	0.036 ( $\pm 0.013$ ) ( $\lambda = 590$ nm)	0.034 ( $\pm 0.008$ ) ( $E = -0.632$ V)	0.049 ( $\pm 0.013$ ) ( $\lambda = 550$ nm)	0.042 ( $\pm 0.008$ ) ( $E = -0.484$ V)
2.50	6.3	0.056 ( $\pm 0.013$ ) ( $\lambda = 600$ nm)	0.062 ( $\pm 0.009$ ) ( $E = -0.590$ V)	0.069 ( $\pm 0.013$ ) ( $\lambda = 536$ nm)	0.071 ( $\pm 0.009$ ) ( $E = -0.504$ V)
2.00	20.0	0.297 ( $\pm 0.010$ ) ( $\lambda = 610$ nm)	0.275 ( $\pm 0.032$ ) ( $E = -0.576$ V)	<i>b</i>	0.307 ( $\pm 0.010$ ) ( $E = -0.436$ V)

<sup>a</sup> $[\text{POM}] = 5 \times 10^{-4} \text{ mol L}^{-1}$ . <sup>b</sup>The absence of isosbestic points was noted. We observed only a decrease of the intensity of the absorbance, which does not allow us to calculate the apparent constant of appearance. Only the kinetic constant of disappearance of  $\beta\beta$ - $\text{Co}_4(\text{P}_2\text{W}_{15})_2$  can be obtained.

We observe a significant variation of the absorbance versus time with a hypsochromic shift of the maximum of absorbance (Figure 7A).



**Figure 7.** (A) Evolution of  $\beta\beta$ - $\text{Co}_4(\text{P}_2\text{W}_{15})_2$  followed by UV–visible spectroscopy. (B) Plots of  $+\ln\{[A(t) - A(\infty)]/[A(0) - A(\infty)]\}$  (red line) and  $-\ln\{[A(t) - A(\infty)]/[A(0) - A(\infty)]\}$  (blue line) versus time at  $\lambda = 600$  and  $536$  nm, respectively. For more clarity, because similar slopes are observed at  $600$  and  $536$  nm,  $-\ln\{[A(t) - A(\infty)]/[A(0) - A(\infty)]\}$  versus time (min) is plotted for  $\lambda = 536$  nm (blue line).  $0.5 \text{ mmol L}^{-1} \beta\beta$ - $\text{Co}_4\text{P}_4\text{W}_{30}$  in  $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4/\text{H}_2\text{SO}_4$  at pH 2.5.

Analysis of the kinetic data was performed at  $\lambda = 600$  and  $536$  nm. The plot of  $[A(t) - A(\infty)]$  versus time shows respectively an exponential decrease and increase of the absorbance. The logarithmic treatment  $\pm \ln\{[A(t) - A(\infty)]/[A(0) - A(\infty)]\} = f(t)$  (Figure 7B) agrees also with a pseudo-first-order reaction, allowing one to measure the apparent kinetic constants  $k_{\text{app}}^-$  and  $k_{\text{app}}^+$ .

The measured values are in agreement to those obtained by electrochemistry, with  $k_{\text{app}}^+ = 0.069 \pm 0.013 \text{ min}^{-1}$  and  $k_{\text{app}}^- = 0.056 \pm 0.013 \text{ min}^{-1}$  at pH 2.5. Varying the pH shows that the reaction is more rapid at lower pH, which is in agreement with the electrochemical study (Table 3).

According to the NMR data, at these low concentrations, the final species is  $\text{Na}_2\text{Co}_2(\text{P}_2\text{W}_{15})_2$  (mixture of isomers; see above). Thus, when  $\text{Co}_4(\text{P}_2\text{W}_{15})_2$  is less concentrated than  $\text{H}_3\text{O}^+$ , we observe decomplexation of the external  $\text{Co}^{2+}$  cations. Consequently, the  $[\text{H}_3\text{O}^+]/[\text{Co}_4(\text{P}_2\text{W}_{15})_2]$  ratio plays a paramount role for the complexation/decomplexation process (see Table 3). These results agree with a series of successive equilibria, allowing one to pass from saturated compound  $\text{Co}_4(\text{P}_2\text{W}_{15})_2$  to mono- and bilacunary complexes  $\text{NaCo}_3(\text{P}_2\text{W}_{15})_2$  and  $\text{Na}_2\text{Co}_2(\text{P}_2\text{W}_{15})_2$  (see Scheme 3).

## CONCLUSION

In this work, we first report interconversion between  $\alpha\beta$ - $\text{Co}_4(\text{P}_2\text{W}_{15})_2$  and  $\beta\beta$ - $\text{Co}_4(\text{P}_2\text{W}_{15})_2$  at pH < 3.5 and a concentration of  $2 \times 10^{-2} \text{ mol L}^{-1}$ , where only the  $\text{NaCo}_3(\text{P}_2\text{W}_{15})_2$  intermediate has been observed by  $^{31}\text{P}$  NMR spectroscopy.

At pH < 3.5 and in diluted solution ( $c = 0.5 \times 10^{-4} \text{ mol L}^{-1}$ ), a decomplexation process of  $\text{Co}_4(\text{P}_2\text{W}_{15})_2$  leads to the formation of isomers of  $\text{NaCo}_3(\text{P}_2\text{W}_{15})_2$  and  $\text{Na}_2\text{Co}_2(\text{P}_2\text{W}_{15})_2$ . This process has been followed at various pH values by electrochemistry, UV–visible spectroscopy, and  $^{31}\text{P}$  NMR spectroscopy. Kinetic parameters are extracted from the electrochemistry and UV–visible experiments and are similar according to accuracy. The kinetic constant of cobalt eviction increases with decreasing pH.

As a result, it appears that both the pH and concentration of  $\text{H}_3\text{O}^+$  and  $\text{Co}_4(\text{P}_2\text{W}_{15})_2$  are of paramount importance in determining the direction of the reaction: when  $\text{Co}_4(\text{P}_2\text{W}_{15})_2$  is less concentrated than  $\text{H}_3\text{O}^+$ , decomplexation of the external  $\text{Co}^{2+}$  cations is observed, while at  $2.5 < \text{pH} < 3.5$  and a high concentration of the unsymmetrical tetracobalt Dawson sandwich complex, only interconversion between  $\alpha\beta$ - $\text{Co}_4(\text{P}_2\text{W}_{15})_2$  and  $\beta\beta$ - $\text{Co}_4(\text{P}_2\text{W}_{15})_2$  is observed.

These results agree with the presence of successive equilibria between saturated compound  $\text{Co}_4\text{P}_4\text{W}_{30}$  and mono- and bilacunary complexes.

## EXPERIMENTAL SECTION

**General Comment.** Most of the common laboratory chemicals were reagent-grade, were purchased from commercial sources, and were used without further purification.



**Preparation of the Compounds.** The potassium salt of  $\alpha$ -[P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>]<sup>6-</sup> and the sodium salt of  $\alpha$ -[P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>]<sup>12-</sup> were prepared by published methods.<sup>22</sup>

$\beta\beta$ -Na<sub>16</sub>[Co<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>)<sub>2</sub>]·60H<sub>2</sub>O,  $\alpha\beta$ -Na<sub>16</sub>[Co<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>)<sub>2</sub>]·51H<sub>2</sub>O·2NaCl, Na<sub>18</sub>[Na<sub>2</sub>Co<sub>2</sub>(P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>)<sub>2</sub>]·57H<sub>2</sub>O (1), and Na<sub>17</sub>[NaCo<sub>3</sub>(P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>)<sub>2</sub>]·48H<sub>2</sub>O (2). These complexes were obtained as previously described.<sup>10,18,19</sup>

**NMR.** <sup>31</sup>P NMR spectra were recorded in 5-mm-o.d. tubes on a Bruker AC 300 apparatus operating at 121.5 MHz in Fourier transform mode (equipped with a QNP probe for <sup>31</sup>P NMR). The <sup>31</sup>P chemical shifts were measured at 300 K on 2 × 10<sup>-2</sup> mol L<sup>-1</sup> solutions of the polyanions in aqueous D<sub>2</sub>O/H<sub>2</sub>O (1:2) in a 0.5 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> solution and were referenced to external 85% H<sub>3</sub>PO<sub>4</sub> (IUPAC convention) by the substitution method. Optical absorption spectra were recorded with a Shimadzu UV 2101 PC spectrophotometer.

**Electrochemical Experiments.** Water used for all electrochemical measurements was obtained by passing through a Milli-RO<sub>4</sub> unit and subsequently through a Millipore Q water purification set. H<sub>2</sub>SO<sub>4</sub> solutions and solid Na<sub>2</sub>SO<sub>4</sub> were commercial products (Prolabo). The electrolyte was made up from a 0.5 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> aqueous solution, and its pH was precisely adjusted to 2.5 by the addition of a 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> + Na<sub>2</sub>SO<sub>4</sub> aqueous solution. Other pH values were adjusted by the addition of either H<sub>2</sub>SO<sub>4</sub> or NaOH (Prolabo). The solutions were deaerated thoroughly for at least 30 min by bubbling with argon (Ar-U from Air Liquide) and kept under an argon atmosphere during the whole experiment.

The glassy carbon samples had a diameter of 3 mm. The electrochemical setup was an EG&G 273A instrument driven by a PC with 270 software. Potentials are quoted against a SCE. The counter electrode was a platinum wire. All voltammetric experiments were carried out at room temperature.

In DPV, current measurements are recorded prior to the pulse and at the end of the pulse. The difference between the two current measurements versus the applied potential results in a differential pulse voltammogram with a peak-shape response. The half-wave potential is calculated using the peak potential value, E<sub>p</sub> (eq 1).

$$E_{1/2} = E_p \pm \Delta E_p/2 \quad (1)$$

where E<sub>p</sub> is the peak potential (V) and ΔE<sub>p</sub> is the pulse amplitude (V). For a reversible system, the peak current may be described by eq 2.

$$\Delta i = nFAD^{1/2}C(\pi t_p)^{-1/2}(1 - \sigma)(1 + \sigma)^{-1} \quad (2)$$

where Δi is the peak current (A), t<sub>p</sub> is the pulse period (s), and σ is the pulse height = exp[(nF/RT)(ΔE<sub>p</sub>/2)].

The peak width at a value of half of the peak current, W<sub>1/2</sub>, follows the relationship of eq 3 for a waveform with a small amplitude pulse applied. W<sub>1/2</sub> has a value of 0.0904/n (V) for a reversible process at 25 °C.

$$W_{1/2} = 3.25RT/nF \quad (3)$$

where W<sub>1/2</sub> is the width of the peak at a current equal to half of the peak current (V).

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### Notes

The authors declare no competing financial interest.

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