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Ferrocenylphosphonic acid: from molecule to electro-active hybrid materials

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Abstract

The reaction of the ferrocenylphosphonic acid with cadmium and manganese nitrate leads as a function of the pH of the initial solution to two types of composition $M(\text{HO}_3\text{Pfc})_2 \cdot x \text{H}_2\text{O}$ and $M(\text{O}_3\text{Pfc})_2 \cdot 2 \text{H}_2\text{O}$. For each composition the iso-structurality of the compounds has been evidenced. The half wave potential of the ferrocene/ferrocenium couple in these systems depends on the degree of neutralization of the ferrocenylphosphonic acid and not on the nature of the metal. **To cite this article:** O. Oms et al., *C. R. Chimie* 8(2005).

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Résumé

La réaction de l'acide ferrocénylphosphonique avec le nitrate de cadmium et de manganèse conduit à deux types de composition $M(\text{HO}_3\text{Pfc})_2 \cdot x \text{H}_2\text{O}$ et $M(\text{O}_3\text{Pfc})_2 \cdot 2 \text{H}_2\text{O}$ en fonction du pH. L'iso-structurality de chacune des compositions a été mise en évidence. Le potentiel de demi-vague du couple ferrocène/ferrocénium de ces systèmes dépend du degré de neutralisation de l'acide ferrocénylphosphonique et non pas de la nature du métal. **Pour citer cet article :** O. Oms et al., *C. R. Chimie* 8(2005). © 2005 Académie des sciences. Published by Elsevier SAS. All rights reserved.

Keywords: Ferrocenylphosphonic acid; Cadmium phosphonate; Manganese phosphonate; Cyclic voltammetry

Mots clés : Acide ferrocénylphosphonique ; Phosphonate de cadmium ; Phosphonate de manganèse ; Voltamétrie cyclique

1. Introduction

Ferrocene and ferrocenyl derivatives are well known for their ability to undergo reversible one-electron oxidation [1]. The redox potential depends on the elec-

tronic effect of the ring substituents on ferrocene. This change of the redox potential of the ferrocenyl center with the electronic effect of the substituent (chelating ligand) has been used to electrochemically sense a neutral or ionic guest molecule allowing its amperometric or potentiometric titration [1–5]. Phosphonic acids are known to react with metal salts to form organic–inorganic metal phosphonates, containing stable PO–

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metal bonds, with usually a two dimensional network [6]; they have also been used as grafting molecules [6]. For example, ferrocenylmethylphosphonic acid has been attached to a silicon surface as a charge storage molecule for memory applications [7].

In this paper we report the preparation and characterization of electro-active cadmium and manganese ferrocenylphosphonates.

2. Results and discussion

Ferrocenylphosphonic acid was prepared using $t\text{BuLi}/t\text{BuOK}$ as a ‘super base’, according to Fig. 1 [8].

The pK_a of the ferrocenylphosphonic acid determined by potentiometry, ^{31}P NMR and by voltammetry are reported in Table 1 [9]. The pK_{a1} of the ferrocenylphosphonic acid cannot be determined by the potentiometric method due to its low solubility in acidic media. The low solubility of the ferrocenylphosphonic acid does not allow the control of the ionic strength of the solution ($C = 0.01 \text{ mol l}^{-1}$) in the potentiometric and NMR experiments. However, the values obtained for pK_{a2} by the potentiometric and ^{31}P NMR methods are in good agreement. The higher values found by the voltammetric method should be attributed to the ionic strength of the medium which was

Table 1
pK values of ferrocenylphosphonic acid

Method	pK_{a1}	pK_{a2}	pK'_{a1}	pK'_{a2}
Potentiometric	< 3	8.3		
^{31}P NMR	2.1	8.3		
Voltammetric	2.4	9.1	1.0	6.2

maintained constant in this method. It is noteworthy that the oxidized forms of the ferrocenylphosphonic acid (pK'_a) are more acidic than the reduced form, as previously observed for ferrocenyl pH-responsive compounds [10,11].

Temperature 20°C , in H_2O , no control of the ionic strength except for the voltammetric method, $\text{KCl } 0.1 \text{ N}$.

Fig. 2 shows the calculated mole fraction α of each ionic species of FcPO_3H_2 and of the oxidized form $\text{Fc}^+\text{PO}_3\text{H}_2$.

2.1. Preparation of cadmium and manganese ferrocenylphosphonates at $pK_{a1} < \text{pH} < pK_{a2}$

The reaction of ferrocenylphosphonic acid with cadmium and manganese nitrates was studied as a function of the initial pH of the solution.

For $pK_{a1} < \text{pH} < pK_{a2}$, the general formula $\text{M}(\text{HO}_3\text{Pfc})_2 \cdot x \text{H}_2\text{O}$ was obtained (Fig. 3).

The compounds were characterized by IR spectroscopy, TGA, ^{31}P and ^{113}Cd MAS NMR, and X-ray analysis.

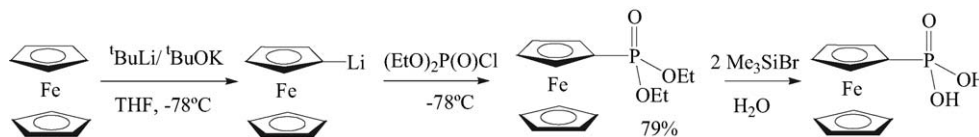


Fig. 1. Preparation of ferrocenylphosphonic acid.

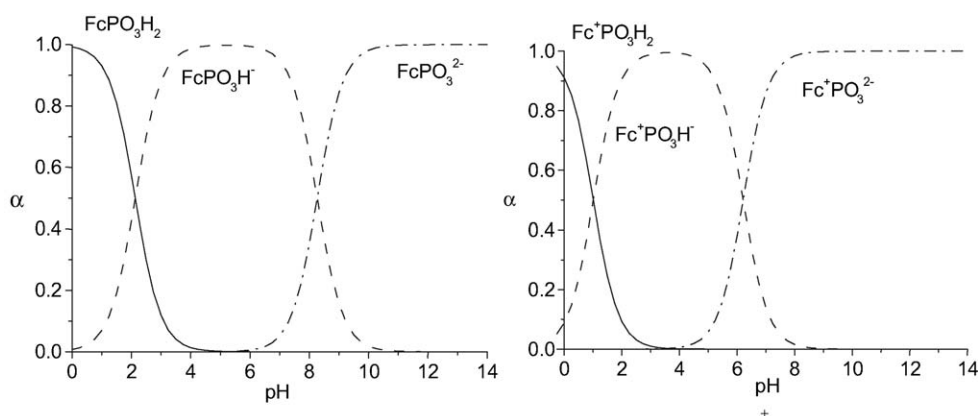


Fig. 2. Mole fraction (α) of ionic species of FcPO_3H_2 and $\text{Fc}^+\text{PO}_3\text{H}_2$.

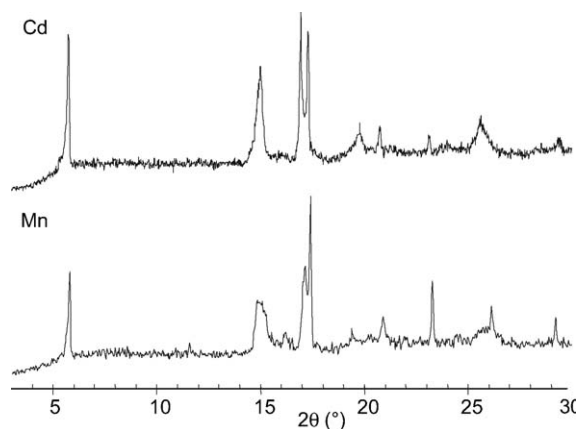


Fig. 6. X-ray patterns of $\text{Cd}(\text{HO}_3\text{PFC})_2 \cdot 3.5 \text{H}_2\text{O}$ and $\text{Mn}(\text{HO}_3\text{PFC})_2 \cdot 3 \text{H}_2\text{O}$.

The diamagnetic compound, $\text{Cd}(\text{O}_3\text{PFC})_2 \cdot 2 \text{H}_2\text{O}$, presents a unique peak in the ^{31}P NMR spectrum at $\delta = 23$ ppm as well in the ^{113}Cd MAS NMR spectrum, with a chemical shift at 15.2 ppm vs. $\text{Cd}(\text{ClO}_4)_2$ 1 M corresponding to hexacoordinated Cd [12,13]. This implies that the oxygen atoms of the phosphonate groups act as bridges between two cadmium atoms ($\mu_2\text{O}$).

The X-ray diffraction patterns of the two compounds are similar as shown in Fig. 10.

From these results the iso-structurality of $\text{Cd}(\text{O}_3\text{PFC})_2 \cdot 2 \text{H}_2\text{O}$ and $\text{Mn}(\text{O}_3\text{PFC})_2 \cdot 2 \text{H}_2\text{O}$ can also be assumed.

2.3. Electrochemical study of the cadmium and manganese ferrocenylphosphonates

Due to the insolubility of the compounds in any solvent, the electrochemical study of these compounds by cyclic voltammetry was performed in the solid state using a cavity microelectrode provided by the 'réseau micro electrode à cavité du CNRS' (France) [14–18]. The results are shown in Table 2. The half wave potential of the ferrocenyl group for the same composition of the metal phosphonates does not depend on the nature

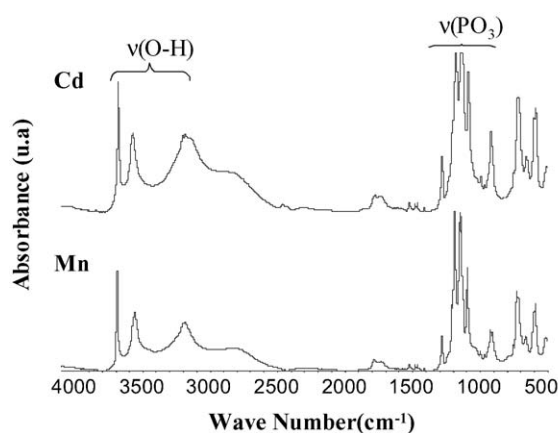


Fig. 8. Ir spectra of $\text{Cd}(\text{O}_3\text{PFC})_2 \cdot 2 \text{H}_2\text{O}$ and $\text{Mn}(\text{O}_3\text{PFC})_2 \cdot 2 \text{H}_2\text{O}$.

of the metal (Zn, Cd, Mn). A maximum in $\Delta E_{1/2}$ of 8 mV is observed between $\text{Zn}(\text{HO}_3\text{PFC})_2 \cdot 2 \text{H}_2\text{O}$ and $\text{Mn}(\text{HO}_3\text{PFC})_2 \cdot 3 \text{H}_2\text{O}$ and 3 mV between $\text{Cd}(\text{O}_3\text{PFC})_2 \cdot 2 \text{H}_2\text{O}$ and $\text{Mn}(\text{O}_3\text{PFC})_2 \cdot 2 \text{H}_2\text{O}$. However the difference between the two compositions, $\text{M}(\text{HO}_3\text{PFC})_2 \cdot x \text{H}_2\text{O}$ and $\text{M}(\text{O}_3\text{PFC})_2 \cdot 2 \text{H}_2\text{O}$ is much more drastic with a $\Delta E_{1/2}$ up to 130 mV. It is noteworthy that the half wave potentials of the metal phosphonates depend on their composition. For $\text{M}(\text{HO}_3\text{PFC})_2$ the half wave potentials are of the same order as the mono sodium salt of ferrocenylphosphonic acid FcPO_3HNa (235–246 mV); while those of $\text{M}(\text{O}_3\text{PFC})_2$ are the same for $\text{M} = \text{Cd}$ or Mn (132–135 mV) but higher than that of the di sodium salt of ferrocenylphosphonic acid FcPO_3Na_2 (86 mV). The half wave potential of the metal ferrocenyl phosphonates does not seem to depend greatly on the nature of the metal but rather on the neutralization of the ferrocenylphosphonic acid.

3. Conclusion

The composition of cadmium and manganese ferrocenylphosphonates, prepared from ferrocenylphosphonic acid and metal nitrate depends on the pH of the initial solution. The cadmium and manganese com-

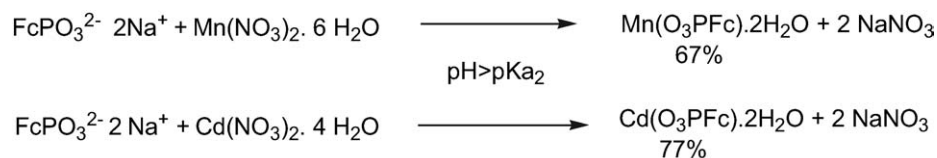


Fig. 7. Preparation of metal ferrocenylphosphonates at $\text{pH} > \text{pK}_{a2}$.

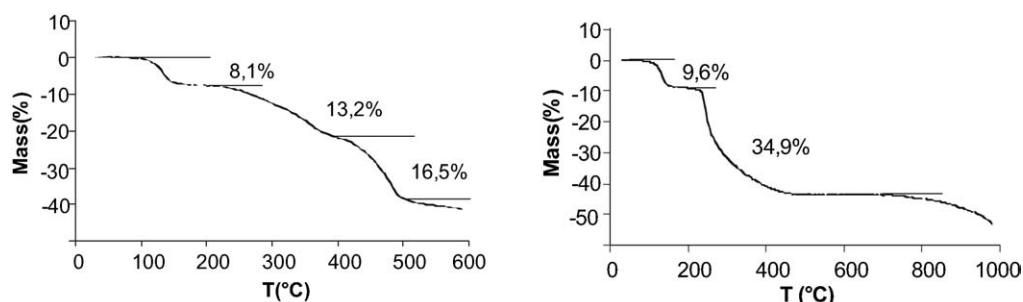


Fig. 9. TGA traces of $\text{Cd}(\text{O}_3\text{PFC})\cdot 2 \text{H}_2\text{O}$ and $\text{Mn}(\text{O}_3\text{PFC})\cdot 2 \text{H}_2\text{O}$ under an inert atmosphere.

pounds are iso-structural. Their half wave potentials are the same for the same composition and do not depend on the nature of the metal. Ferrocenylphosphonic acid does not behave as a metal cation sensor but rather as a pH sensor.

4. Experimental section

IR spectra were performed on a Thermo Nicolet AVATAR 320 FT-IR apparatus as KBr pellets. MAS

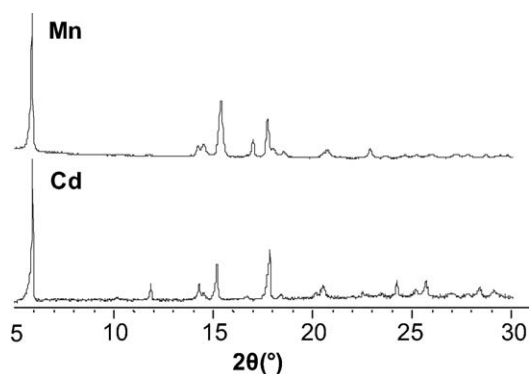


Fig. 10. X-ray diffraction data of $\text{Cd}(\text{O}_3\text{PFC})\cdot 2\text{H}_2\text{O}$ and $\text{Mn}(\text{O}_3\text{PFC})\cdot 2\text{H}_2\text{O}$.

Table 2

Electrochemical data of metal ferrocenylphosphonates at 20 °C in water, electrolyte: KCl 1 M, saturated calomel as reference electrode, scan rate: 100 mV s⁻¹

Compounds	E_{pa} (mV)	E_{pc} (mV)	$E_{1/2}$ (mV)	$\Delta E = E_{\text{pa}} - E_{\text{pc}}$ (mV)
$\text{Zn}(\text{HO}_3\text{PFC})_2\cdot 2 \text{H}_2\text{O}^{\text{a}}$	260	210	235	50
$\text{Cd}(\text{HO}_3\text{PFC})_2\cdot 3.5 \text{H}_2\text{O}$	264	213	238	51
$\text{Mn}(\text{HO}_3\text{PFC})_2\cdot 3 \text{H}_2\text{O}$	270	217	243	53
$\text{Cd}(\text{O}_3\text{PFC})\cdot 2 \text{H}_2\text{O}$	157	107	132	50
$\text{Mn}(\text{O}_3\text{PFC})\cdot 2 \text{H}_2\text{O}$	155	115	135	40
$\text{FcPO}_3\text{H}^-\text{Na}^{+\text{b}}$	281	211	246	70
$\text{FcPO}_3^{2-}\text{2Na}^{+\text{b}}$	119	54	86	65

^a Prepared according to [19].

^b Cyclic voltammogram in solution.

NMR spectra were taken on a Bruker DPX 300 operating at 121.5 MHz for ³¹P and 66.5 MHz for ¹¹³Cd. The reference used were H₃PO₄ 30% for ³¹P and Cd(ClO₄)₂ 1 M for ¹¹³Cd. Powder X-ray diffraction was performed on an X Pert Philips diffractometer. TGA were made on a Netzch 409 thermobalance. Cyclic voltammetry measurements were performed by means of a Radiometer Analytical PGZ 100 potentiostat in a three-electrode cell. A cavity microelectrode with a Pt working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode were used to record voltammograms. The electrolyte was KCl (1 M in water). The scan rate was 100 mV s⁻¹. Elemental analyses were performed by the 'Service central d'analyse' of CNRS in Vernaison, France.

Ferrocenylphosphonic acid and zinc ferrocenylphosphonate $\text{Zn}(\text{HO}_3\text{PFC})\cdot 2 \text{H}_2\text{O}$ have been prepared as already reported [8,19].

4.1. Preparation of $\text{Cd}(\text{HO}_3\text{PFC})_2\cdot 3.5 \text{H}_2\text{O}$

Ferrocenylphosphonic acid (0.098 g, 0.36 mmol) was dissolved in 15 ml of water. The pH was adjusted to 3.7 by addition of NaOH 1 M. Cd(NO₃)₂·4 H₂O (0.11 g, 0.36 mmol) was added to the solution without

stirring. After 5 days at room temperature, the yellow precipitate was filtered, washed with methanol and ether, and dried under vacuum leading to 66 mg (0.09 mmol) of $\text{Cd}(\text{HO}_3\text{PFC})_2 \cdot 3.5\text{H}_2\text{O}$ (53% yield). ^{31}P MAS NMR, 18.1 ppm; ^{113}Cd MAS NMR, -18.2 ppm vs. $\text{Cd}(\text{ClO}_4)_2$ 1 M. Anal. Calc. for $\text{CdP}_2\text{Fe}_2\text{C}_{20}\text{H}_{27}\text{O}_{9.5}$: Cd, 15.93%; Fe, 15.83%; P, 8.78%; C, 34.02%; H 3.83%; found: Cd, 15.10%; Fe, 15.40%; P, 8.43%; C, 33.68%; H, 3.80%.

4.2. Preparation of $\text{Cd}(\text{O}_3\text{PFC})_2 \cdot 2\text{H}_2\text{O}$

Ferrocenylphosphonic acid (0.1 g, 0.38 mmol) was dissolved in 28 ml of water. The pH was adjusted to 10.2 by addition of NaOH 1 M. $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.12 g, 0.39 mmol) was added to the solution without stirring. After 5 days at room temperature, the yellow precipitate was filtered, washed with methanol and ether, and dried under vacuum leading to 120 mg (0.29 mmol) of $\text{Cd}(\text{O}_3\text{PFC})_2 \cdot 2\text{H}_2\text{O}$ (77% yield). ^{31}P MAS NMR, 23.4 ppm; ^{113}Cd MAS NMR, 15.2 ppm vs. $\text{Cd}(\text{ClO}_4)_2$ 1 M. Anal. Calc. for $\text{CdP}_2\text{Fe}_2\text{C}_{10}\text{H}_{13}\text{O}_5$: Cd, 27.26%; P, 7.44%; Fe, 13.24%; found: Cd, 26.61%; P, 7.52%; Fe, 13.50%.

4.3. Preparation of $\text{Mn}(\text{HO}_3\text{PFC})_2 \cdot 3\text{H}_2\text{O}$

Ferrocenylphosphonic acid (0.15 g, 0.56 mmol) was dissolved in 35 ml of water. The pH was adjusted to 3.5 by addition of NaOH 1 M. $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.08 g, 0.32 mmol) was added to the solution without stirring. After 5 days at room temperature, the yellow precipitate was filtered, washed with methanol and ether, and dried under vacuum leading to 95 mg (0.15 mmol) of $\text{Mn}(\text{HO}_3\text{PFC})_2 \cdot 3\text{H}_2\text{O}$ (53% yield). Anal. Calc. for $\text{MnP}_2\text{Fe}_2\text{C}_{20}\text{H}_{26}\text{O}_9$: Mn, 8.60%; P, 9.71%; Fe, 17.49%; C, 37.58%; H, 4.07%; found: Mn, 8.46%; P, 9.58%; Fe, 17.62%; C, 38.56%; H, 3.60%.

4.4. Preparation of $\text{Mn}(\text{O}_3\text{PFC})_2 \cdot 2\text{H}_2\text{O}$

Ferrocenylphosphonic acid (0.10 g, 0.38 mmol) was dissolved in 28 ml of water. The pH was adjusted to 11 by addition of NaOH 1 M. $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.09 g, 0.36 mmol) was added to the solution without stirring.

After 5 days at room temperature, the yellow precipitate was filtered, washed with methanol and ether, and dried under vacuum leading to 86 mg (0.24 mmol) of $\text{Mn}(\text{O}_3\text{PFC})_2 \cdot 2\text{H}_2\text{O}$ (67% yield). Anal. Calc. for $\text{MnPFeC}_{10}\text{H}_{13}\text{O}_5$: Mn, 15.48%; P, 8.73%; Fe, 15.74%; C, 33.88%; H, 3.66%; found: Mn, 15.11%; P, 8.68%; Fe, 15.57%; C, 33.90%; H, 3.83%.

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