

Structure, Electrochemistry and Magnetism of the Iron(III)-Substituted Keggin

Dimer, $[\text{Fe}_6(\text{OH})_3(\text{A}-\alpha\text{-GeW}_9\text{O}_{34}(\text{OH})_3)_2]^{11-}$

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SUPPORTING INFORMATION

Study of the Electrolyte Effect on the Cyclic Voltammetry of $[\text{Fe}_6(\text{OH})_3(\text{A}-\alpha\text{-GeW}_9\text{O}_{34}(\text{OH})_3)_2]^{11-}$ (1)

The behavior of the Fe^{III} centers was studied at pH 3, as a function of the composition of the supporting electrolyte. As previously,^[1] the pH 3 sulfate solution was selected as the reference medium, with which were compared the media containing perchlorate, chloride, acetate and dihydrogenophosphate, respectively. Three representative examples are shown: they compare the cyclic voltammograms in acetate and sulfate media (Fig. SI1), in acetate and chloride (Fig. SI2) and in acetate and phosphate media (Fig. SI3). In Figures SI1 and SI2, a clear splitting of the Fe-wave in acetate is observed, accompanied by a sharpening and a shift in the positive potential direction of the main reduction peak. The example in the presence of chloride illustrates the buffer capacity effect. The “acetate” pattern was maintained, independent of the potential scan rate within the limits indicated earlier. This composite voltammogram was also observed in acetate medium at pH 4 and 5, with roughly 0.120 V/pH potential negative shift for the main peak. Recently, we have shown that the Fe-wave in the multi-

iron Wells-Dawson complexes, $\alpha\text{-Na}_{11}[\text{X}_2(\text{Fe}^{\text{III}}\text{Cl})_2(\text{Fe}^{\text{III}}\text{OH}_2)\text{W}_{15}\text{O}_{59}]$ ($\text{X} = \text{P}$ or As) could be induced to split, at least partly, by raising the pH from 3 to 5.^[2,3] Therefore, in the present experiments, we wondered whether pH variation with another anion present in the supporting electrolyte could also show the same trend. The result presented in Fig. SI3 compares the cyclic voltammograms for CH_3COO^- and H_2PO_4^- , respectively present in a pH = 5 buffer. The attempt is satisfactory: even though splitting of the Fe-wave is not as complete as observed with CH_3COO^- , a clearly composite wave is obtained with H_2PO_4^- . This observation indicates that the voltammetric pattern is influenced by the interplay between the pK_a values of the complex, the pH of the solution and the nature of the anion present in the electrolyte. It is also consistent with an expected electronic communication between the Fe^{III} centers upon consideration of the structure of the complex.

References

- (1) Keita, B.; Lu, Y. W.; Nadjo, L.; Contant, R. *Eur. J. Inorg. Chem.* **2000**, 2463.
- (2) Kortz, U.; Savelieff, M. G.; Bassil, B. S.; Keita, B.; Nadjo, L. *Inorg. Chem.* **2002**, *41*, 783.
- (3) Keita, B.; Mbomekalle, I. M.; Nadjo, L.; Anderson, T. M.; Hill, C. L. *Inorg. Chem.* **2004**, *43*, 3257.

Figure captions (Supporting Information)

Fig. SI1. Comparison of the cyclic voltammograms, restricted to the Fe-waves for a 2×10^{-4} M solution of **1** in pH = 3 media of different composition:

Full line: sulfate medium (0.2 M $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$)

Dotted line: acetate medium (0.4 M $\text{CH}_3\text{COONa} + \text{ClCH}_2\text{COOH}$)

Working electrode: glassy carbon; reference electrode: SCE; scan rate: $10 \text{ mV}\cdot\text{s}^{-1}$

Fig. SI2. Comparison of the cyclic voltammograms, restricted to the two first waves for a 2×10^{-4} M solution of **1** in pH = 3 media of different composition:

Full line: chloride medium (0.4 M $\text{NaCl} + \text{HCl}$)

Dotted line: acetate medium (0.4 M $\text{CH}_3\text{COONa} + \text{ClCH}_2\text{COOH}$)

Working electrode: glassy carbon; reference electrode: SCE; scan rate: $10 \text{ mV}\cdot\text{s}^{-1}$

Fig. SI3. Comparison of the cyclic voltammograms, restricted to the Fe-waves for a 2×10^{-4} M solution of **1** in pH = 5 media of different composition:

Full line: phosphate medium (0.4 M $\text{NaH}_2\text{PO}_4 + \text{NaOH}$)

Dotted line: acetate medium (0.4 M $\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH}$)

Working electrode: glassy carbon; reference electrode: SCE; scan rate: $10 \text{ mV}\cdot\text{s}^{-1}$

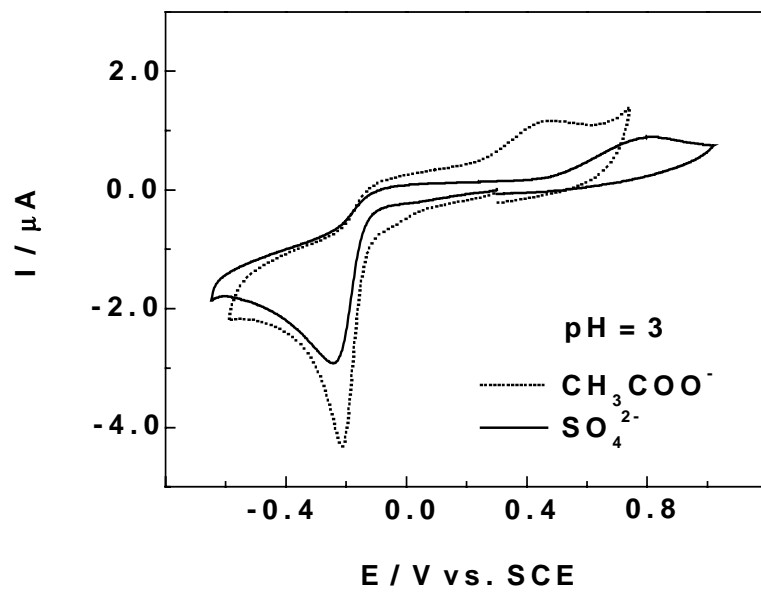


Figure SI1

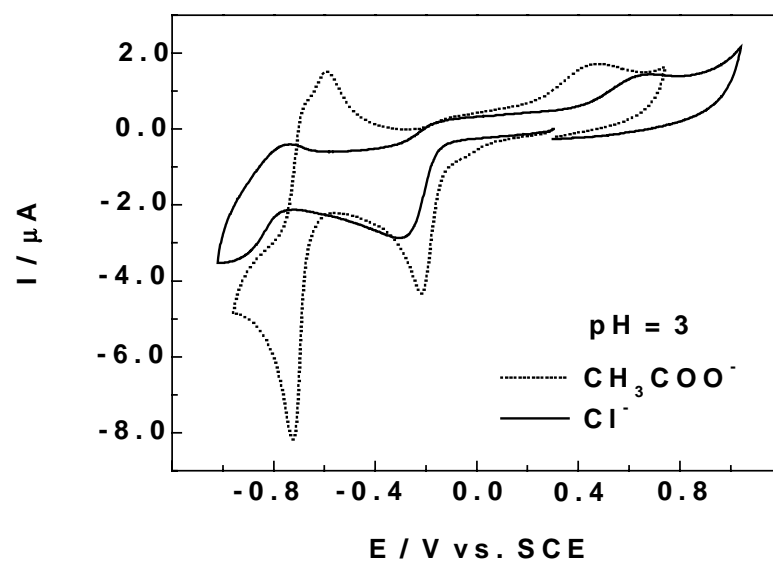


Figure SI2

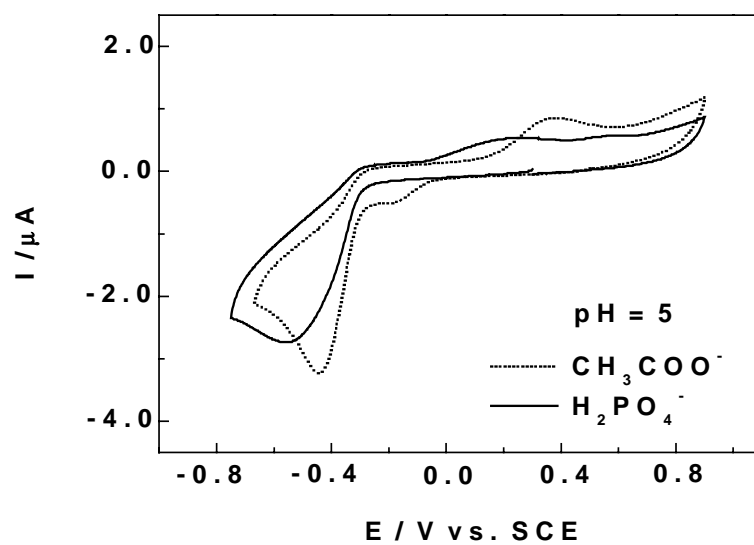


Figure SI3