Supplementary Material



**Fig. S1**. Distribution diagram of the species as a function of pH in a solution containing V3+ ion and acac (VIII/acac = 1/3, VIII = 1.50 × 10–4 M). The stability constants of the VIII–acac complexes were taken from ([Brito et al., 2009](#_ENREF_1)).



**Fig. S2**. ESI-MS spectrum recorded in ultrapure water on the systems containing VIII(acac)3 with V concentration of 150 M, pH 6.3. At these experimental conditions, VIII species partly oxidizes to VIVO.



**Fig. S3**. Experimental (above) and calculated (below) isotopic pattern of the species [VIII(acac)3+H+].



**Fig. S4**. Experimental (above) and calculated (below) isotopic pattern of the species [VIII(acac)3+Na+].



**Fig. S5**. Deconvoluted ESI-MS spectrum recorded on the systems containing VIII(acac)3 and lysozyme with the molar ratio VIII/Protein 3/1 and Protein concentration 5 M, pH 6.5. Under these experimental conditions, VIII species fully oxidizes to VIVO



**Fig. S6**. Deconvoluted ESI-MS spectrum recorded on the systems containing VIVO(acac)2 and lysozyme with the molar ratio VIV/Protein 3/1 and Protein concentration 50 M, pH 6.8.



**Fig. S7**. Low and high-field region of the EPR spectra recorded on frozen solutions (120 K) of the systems: a) VIVO/acac 1/2, pH 4.40; b) VIII(acac)3/Lyz 3/1, pH 4.95; c) VIII(acac)3/Lyz 2/1, pH 5.05 and d) VIVO/acac 1/2, pH 5.75. V concentration was 1 mM. With **I**, **II** and **III** the *M*I = -7/2, +7/2 resonances of the species VIVO(acac)+, [VIVO(acac)]–Lyz and [VIVO(acac)2]–Lyz, are indicated, respectively.



**Fig. S8**. ESI-MS spectra recorded in ultrapure water on the systems containing VV/acac with molar rario 1/2 and with V concentration of 150 M, pH 7.0: a) positive-ion mode and b) negative-ion mode.

**References**

Brito, F., Araujo, M. L., Martínez, J. D., Hernández, Y., Moh, A., and Lubes, V. (2009). Speciation of the vanadium(III)–acetylacetone system in 3.0 M KCl ionic medium at 25°C. *J. Coord. Chem.* 62, 52-62. doi: 10.1080/00958970802474763.