Supplementary Material for the paper

Spectroscopic determination of metal-ligand coordination by biologically active 2-picolinehydroxamic acid with iron(III) and oxidovanadium(IV) in aqueous solutions

Magdalena Woźniczka, Mirosława Świątek, Joanna Gądek-Sobczyńska, Beata Pasternak, Aleksander Kufelnicki

Page 6. **Fig. S5. (a)** Negative-ion ESI–MS spectrum for the complexes formed in the $FeCl_3$/PicHA system at ligand-to-metal molar ratio 4:1, pH 6.5, $c_{Fe(III)} = 2.5 \times 10^{-4}$ mol L^{-1}.

(b) Positive-ion ESI–MS spectrum for the complexes formed in the $FeCl_3$/PicHA system at ligand-to-metal molar ratio 4:1, pH 6.5, $c_{Fe(III)} = 2.5 \times 10^{-4}$ mol L^{-1}. Explanation of the signal described in the text:
m/z = 303.0 [Fe(II) + 2fragment ions m/z = 106 + Cl]$^+$.

Page 7. **Fig. S6.** Positive-ion ESI–MS spectrum for the complexes formed in the $VOSO_4$/PicHA system at ligand-to-metal molar ratio 2:1, pH 1.4, $c_{VO(IV)} = 2.5 \times 10^{-3}$ mol L^{-1}. Explanation of the signals described in the text:
m/z = 282.0 [VOL + fragment ion m/z = 78]$^+$
m/z = 283.0 [L + fragment ion m/z = 122 + Na + H]$^+$
m/z = 326.0 [VOL + fragment ion m/z = 122]$^+$
m/z = 567.0 [$(VO)_2L_2$ + SO_4 + NaOH + Na]$^+$.

Page 8. **Fig. S7** Positive-ion ESI–MS spectrum for the complexes formed in the $VOSO_4$/PicHA system at ligand-to-metal molar ratio 2:1, pH 2.6, $c_{VO(IV)} = 2.5 \times 10^{-3}$ mol L^{-1}.

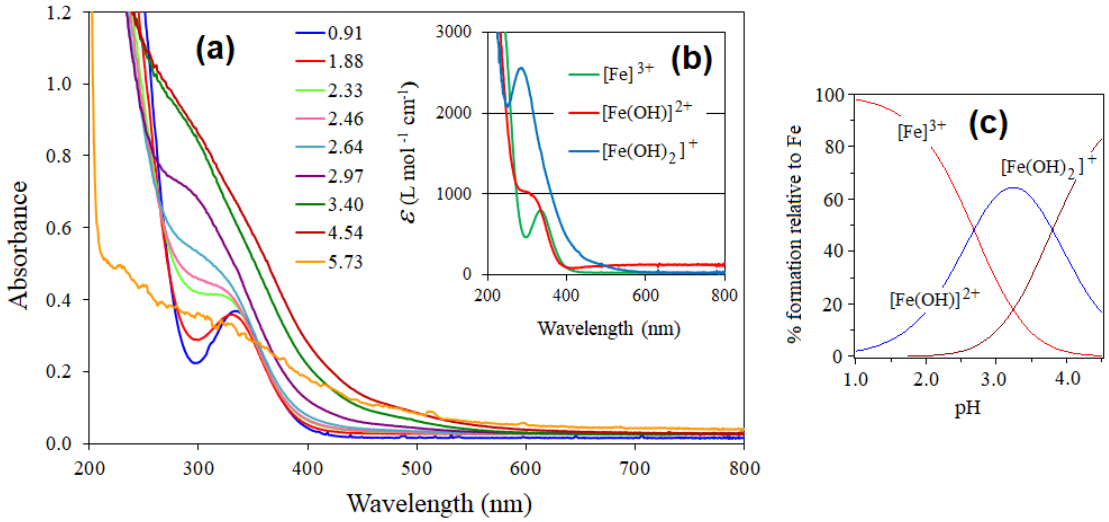

Fig. S1. (a) UV-Vis spectra of iron(III) chloride within the pH range 0.91 – 5.73, c_{FeCl_3} = 5.0 × 10^{-4} mol L^{-1}. **(b)** Molar absorption coefficients for various Fe(III) aqua-hydroxido complexes. **(c)** Species distribution curves as a function of pH for the Fe(III) aqua-hydroxido complexes.

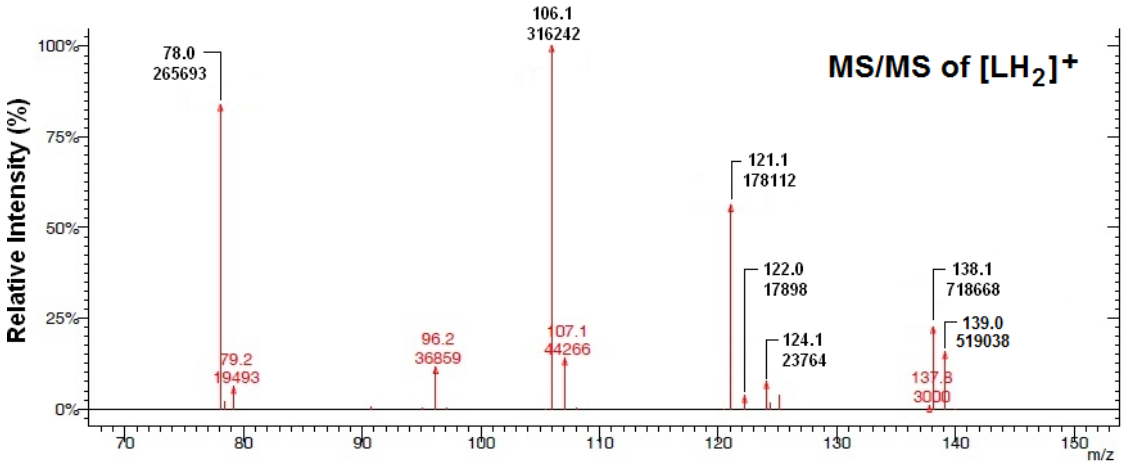

Fig. S2. Tandem mass spectrum of $[LH_2]^+$ – *m/z* = 139.0, c_{PicHA}= 1.0 × 10^{-2} mol L^{-1}.

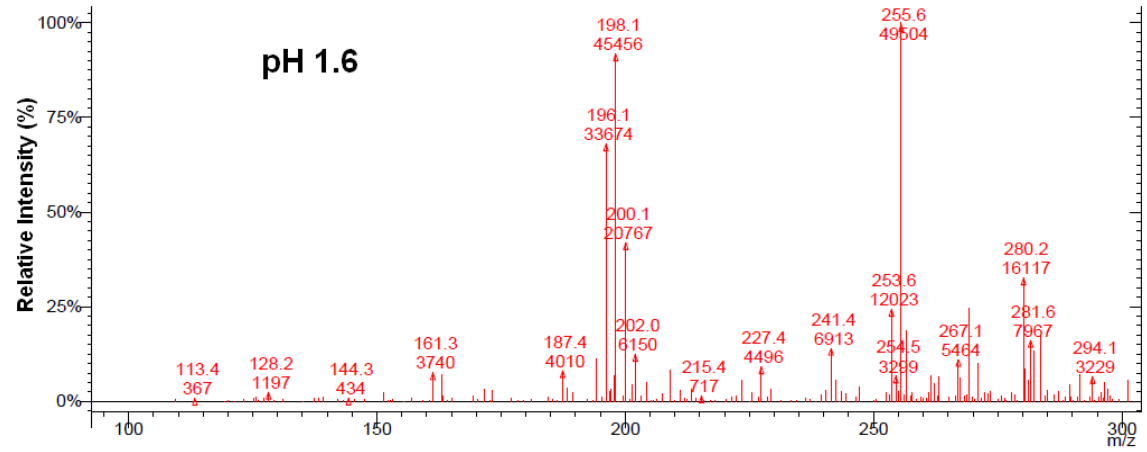

Fig. S3. Negative-ion ESI–MS spectrum for the complexes formed in the $FeCl_3$/PicHA system at ligand-to-metal molar ratio 4:1, pH 1.6, $c_{Fe(III)}$ = 2.5 × 10^{-4} mol L^{-1}. Explanation of the signal described in the text:

m/z = 256.0 [Fe(III) + fragment ion *m/z* = 78 + 3Cl + OH]$^-$.

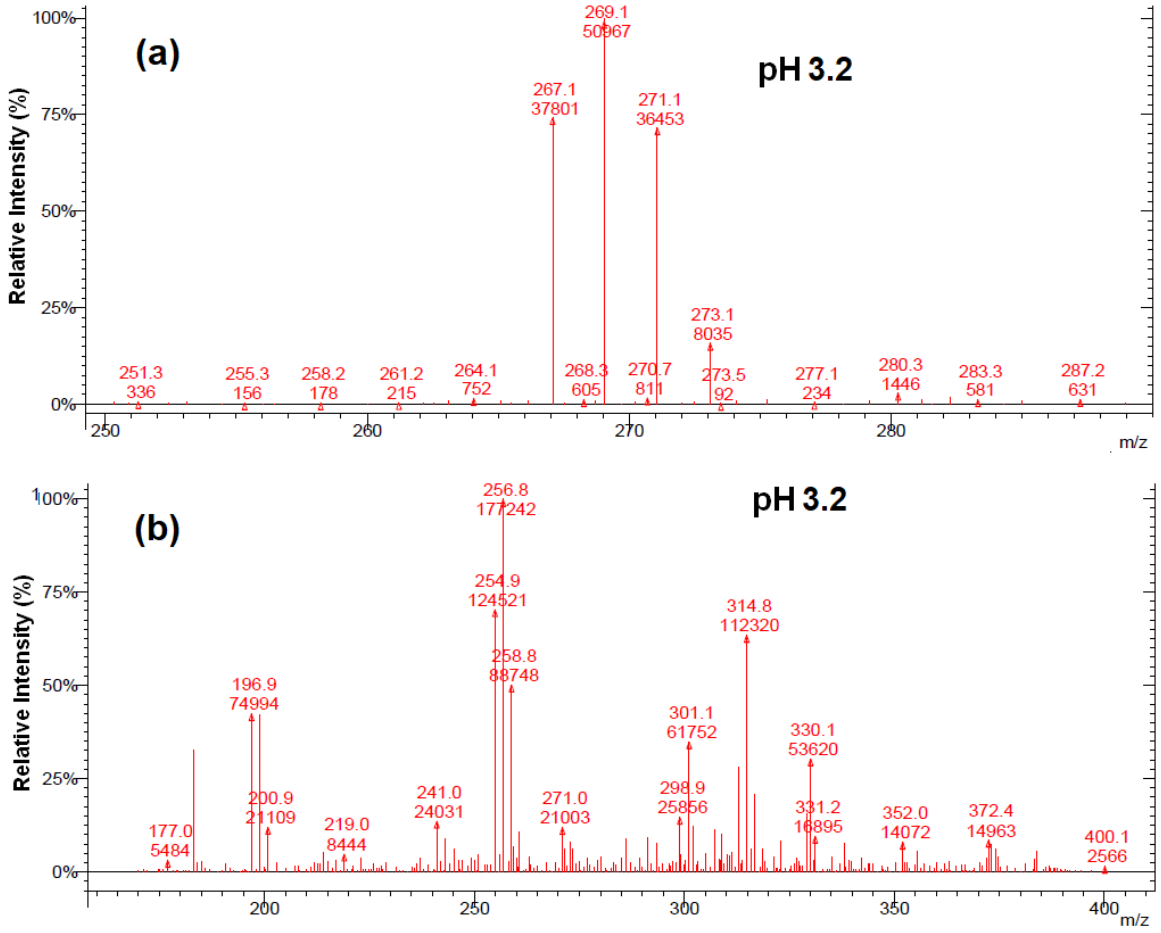

Fig. S4. (a) Negative-ion ESI–MS spectrum for the complexes formed in the $FeCl_3$/PicHA system at ligand-to-metal molar ratio 4:1, pH 3.2, $c_{Fe(III)} = 2.5 \times 10^{-4}$ mol L^{-1}. Explanation of the signal described in the text:

m/z = 269.0 [Fe(II) + fragment ion *m/z* = 122 + NaOH + 3OH]$^-$.

(b) Positive-ion ESI–MS spectrum for the complexes formed in the $FeCl_3$/PicHA system at ligand-to-metal molar ratio 4:1, pH 3.2, $c_{Fe(III)} = 2.5 \times 10^{-4}$ mol L^{-1}. Explanation of the signals described in the text:

m/z = 197.0 [Fe(II) + fragment ion *m/z* = 106+Cl]$^+$

m/z = 255.0 [Fe(II) + fragment ion *m/z* = 106 + NaCl + Cl]$^+$.

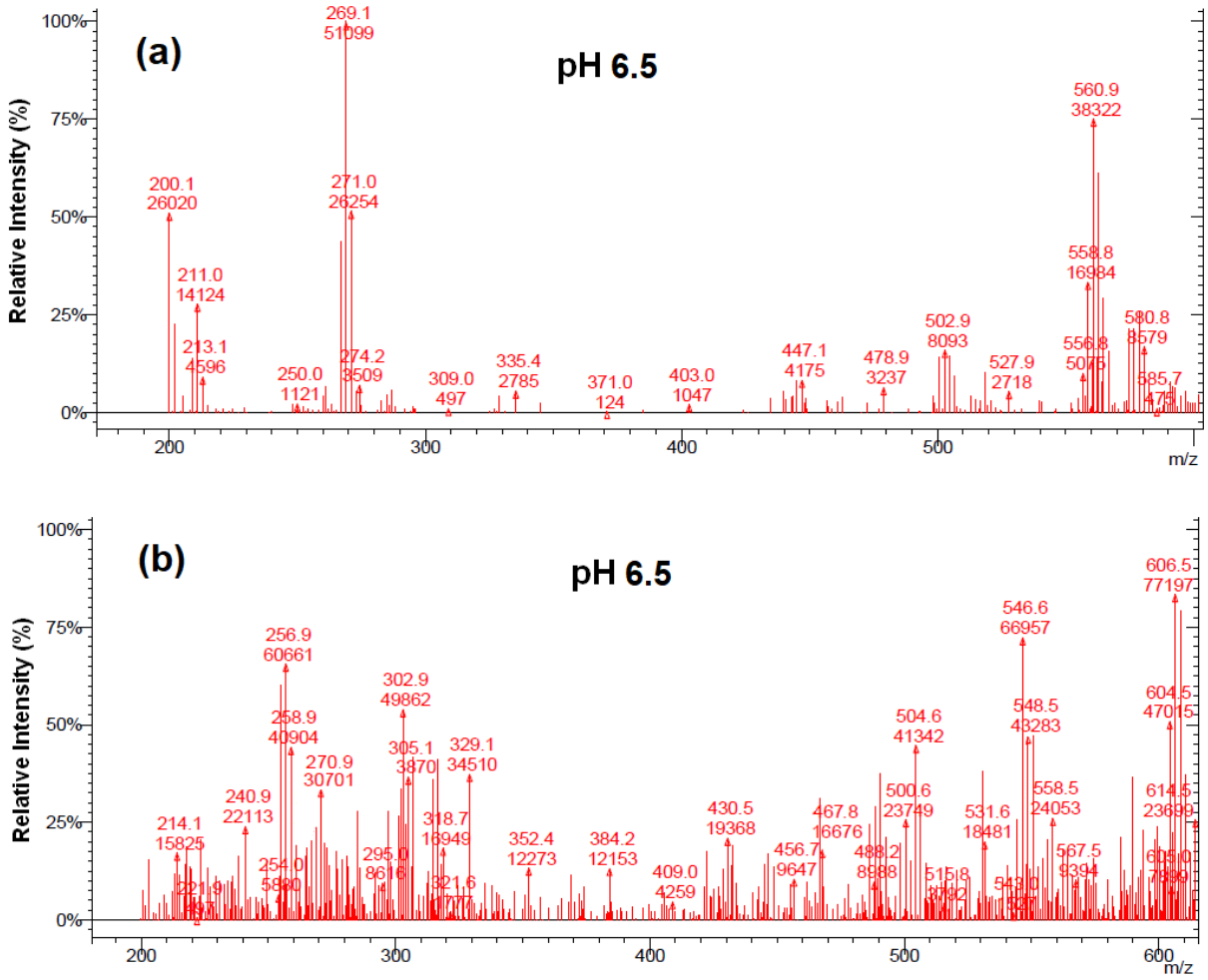

Fig. S5. (a) Negative-ion ESI–MS spectrum for the complexes formed in the $FeCl_3$/PicHA system at ligand-to-metal molar ratio 4:1, pH 6.5, $c_{Fe(III)} = 2.5 \times 10^{-4}$ mol L^{-1}.

(b) Positive-ion ESI–MS spectrum for the complexes formed in the $FeCl_3$/PicHA system at ligand-to-metal molar ratio 4:1, pH 6.5, $c_{Fe(III)} = 2.5 \times 10^{-4}$ mol L^{-1}. Explanation of the signal described in the text:

m/z = 303.0 [Fe(II) + 2fragment ions *m/z* = 106 + Cl]$^+$.

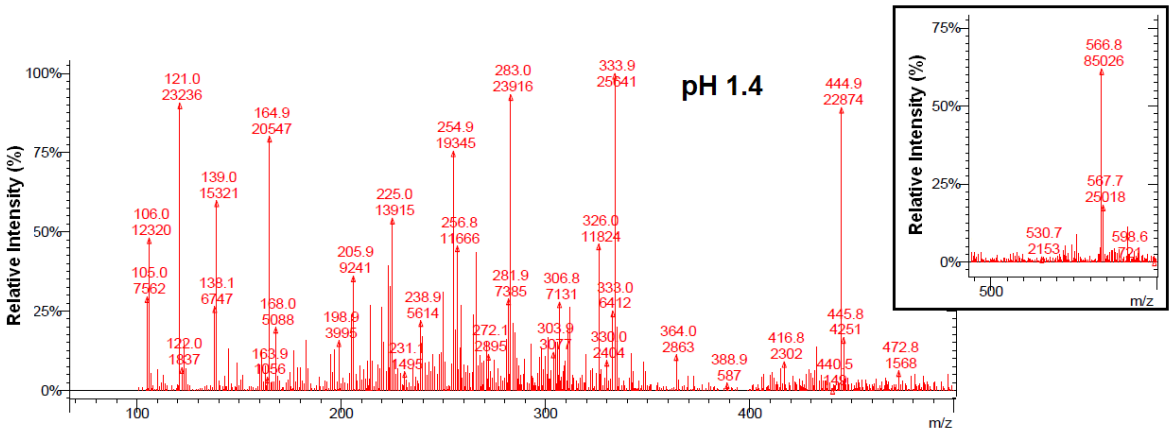

Fig. S6. Positive-ion ESI–MS spectrum for the complexes formed in the $VOSO_4$/PicHA system at ligand-to-metal molar ratio 2:1, pH 1.4, $c_{VO(IV)} = 2.5 \times 10^{-3}$ mol L^{-1}. Explanation of the signals described in the text:

m/z = 282.0 [VOL + fragment ion *m/z* = 78]$^+$

m/z = 283.0 [L + fragment ion *m/z* = 122 + Na + H]$^+$

m/z = 326.0 [VOL + fragment ion *m/z* = 122]$^+$

m/z = 567.0 $[(VO)_2L_2 + SO_4 + NaOH + Na]^+$.

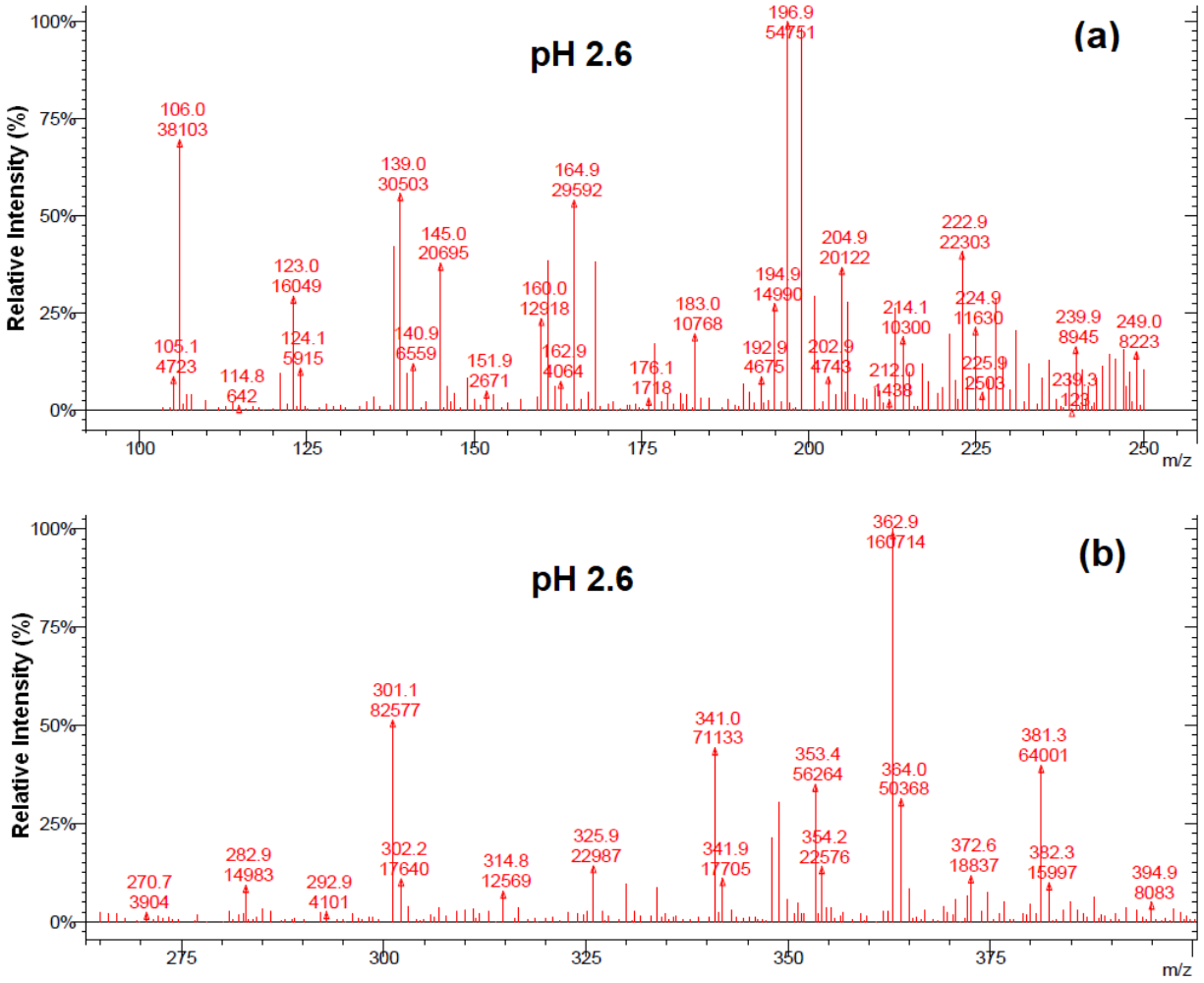

Fig. S7. Positive-ion ESI–MS spectrum for the complexes formed in the $VOSO_4$/PicHA system at ligand-to-metal molar ratio 2:1, pH 2.6, $c_{VO(IV)} = 2.5 \times 10^{-3}$ mol L^{-1}.