Supplementary Material for the paper

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

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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 $L^{-1}$.

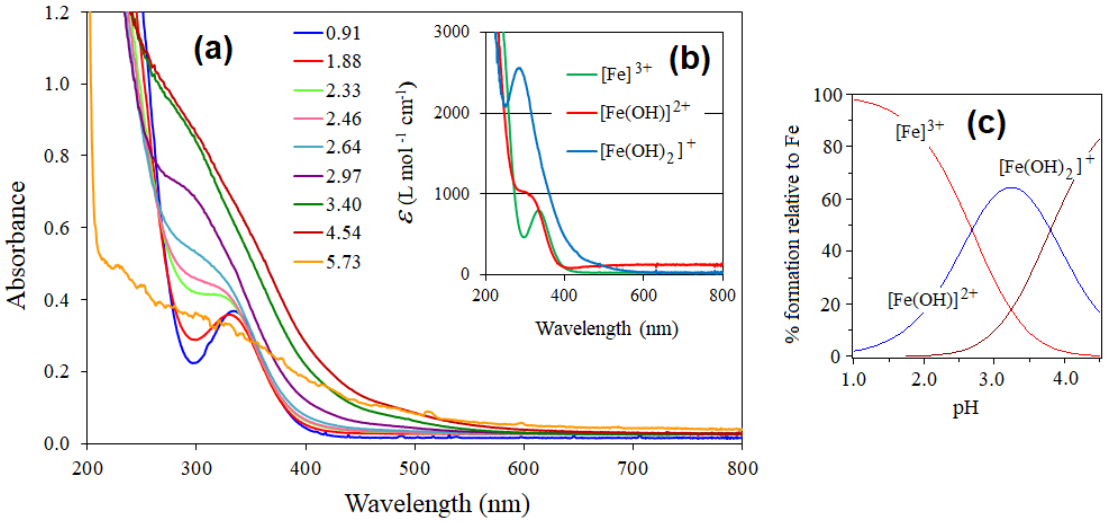


**Fig. S1. (a)** UV-Vis spectra of iron(III) chloride within the pH range 0.91 – 5.73, $C_{FeCl_3}$ = 5.0 × $10^{-4}$ mol $L^{-1}$. **(b)** Molar absorption coefficients for various Fe(III) aqua-hydroxo complexes. **(c)** Species distribution curves as a function of pH for the Fe(III) aqua-hydroxo complexes.

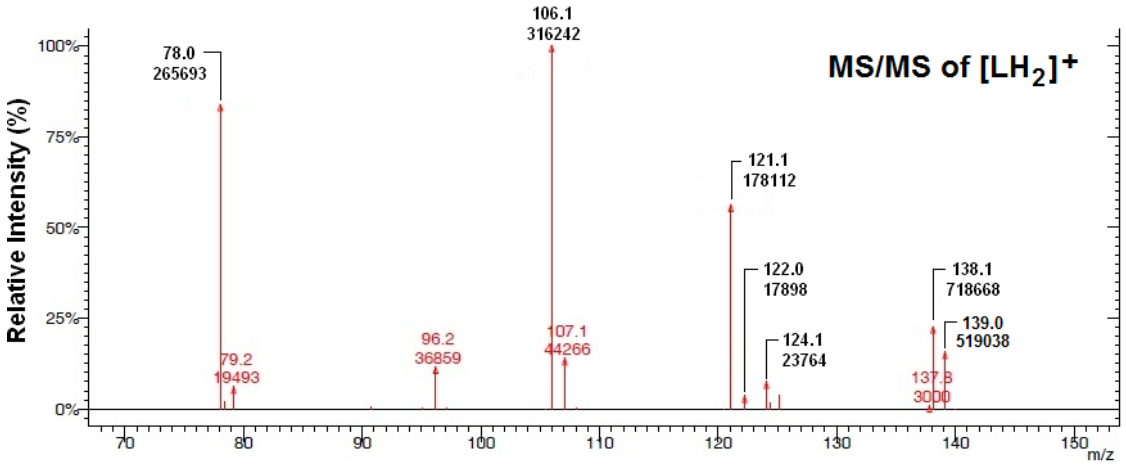


**Fig. S2.** Tandem mass spectrum of $[LH_2]^+$ – *m/z* = 139.0, $C_{PicHA}$= 1.0 × $10^{-2}$ mol $L^{-1}$.

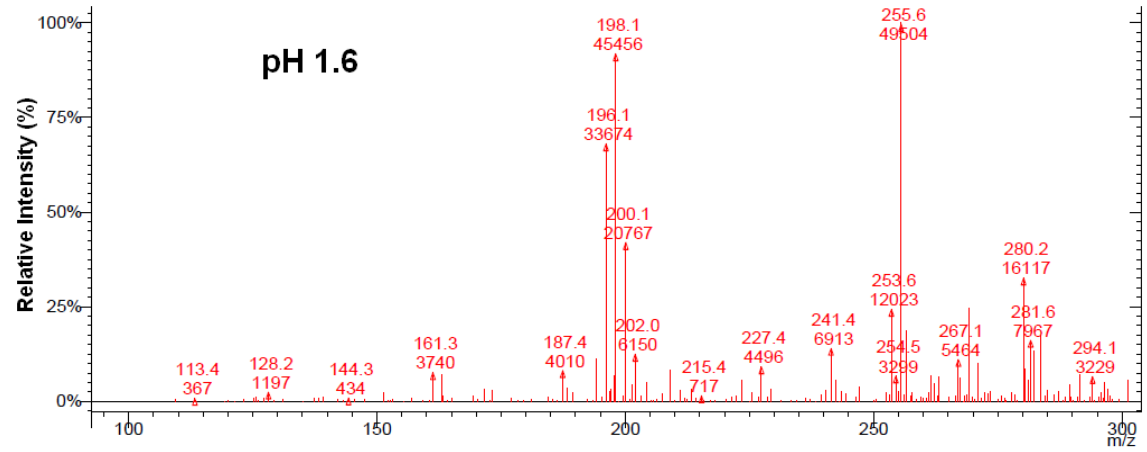


**Fig. S3.** Negative-ion ESI–MS spectrum for the complexes formed in the $FeCl_3$/PicHA system at ligand-to-metal molar ratio 4:1, pH 1.6, $C_{Fe(III)}$ = 2.5 × $10^{-4}$ mol $L^{-1}$. Explanation of the signal described in the text:

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

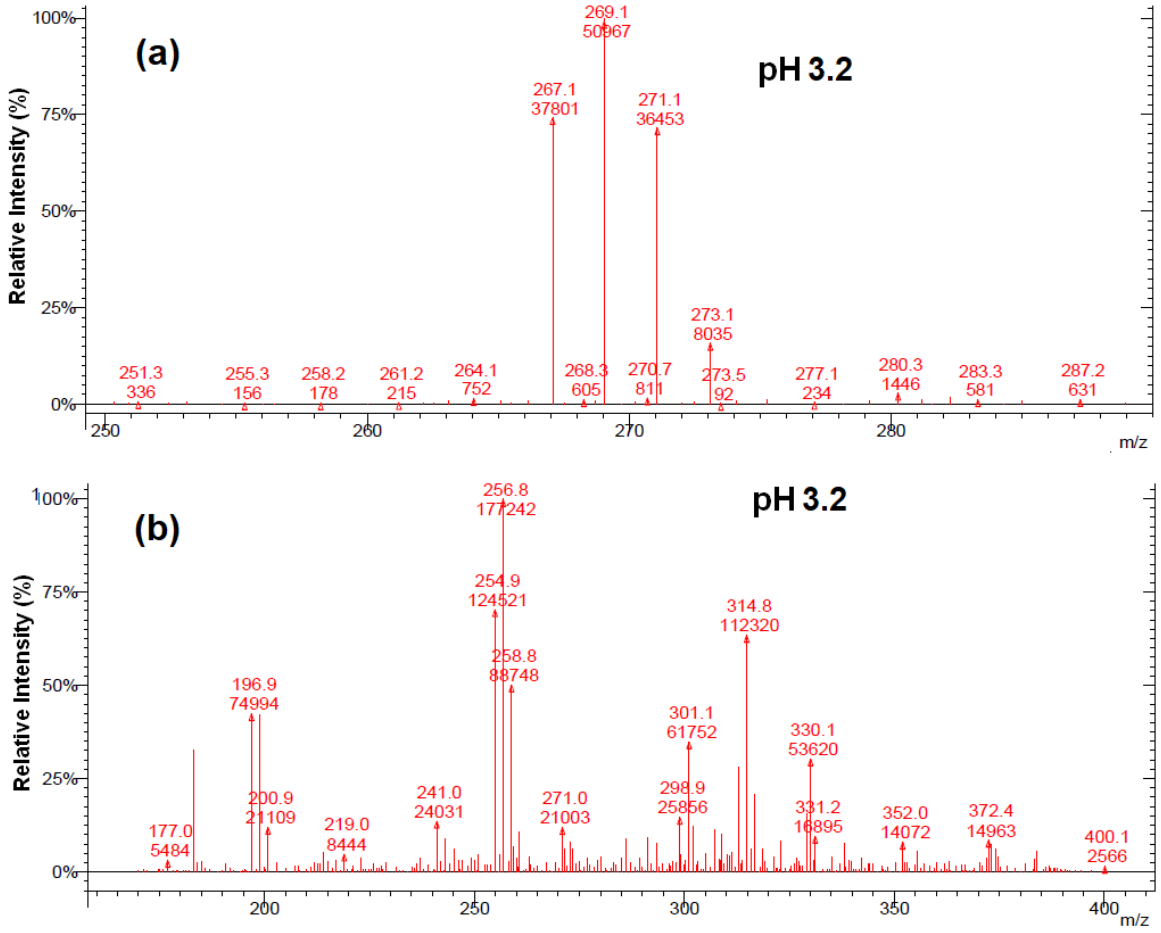


**Fig. S4. (a)** Negative-ion ESI–MS spectrum for the complexes formed in the $FeCl_3$/PicHA system at ligand-to-metal molar ratio 4:1, pH 3.2, $C_{Fe(III)} = 2.5 \times 10^{-4}$ mol $L^{-1}$. Explanation of the signal described in the text:

*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]$^+$.

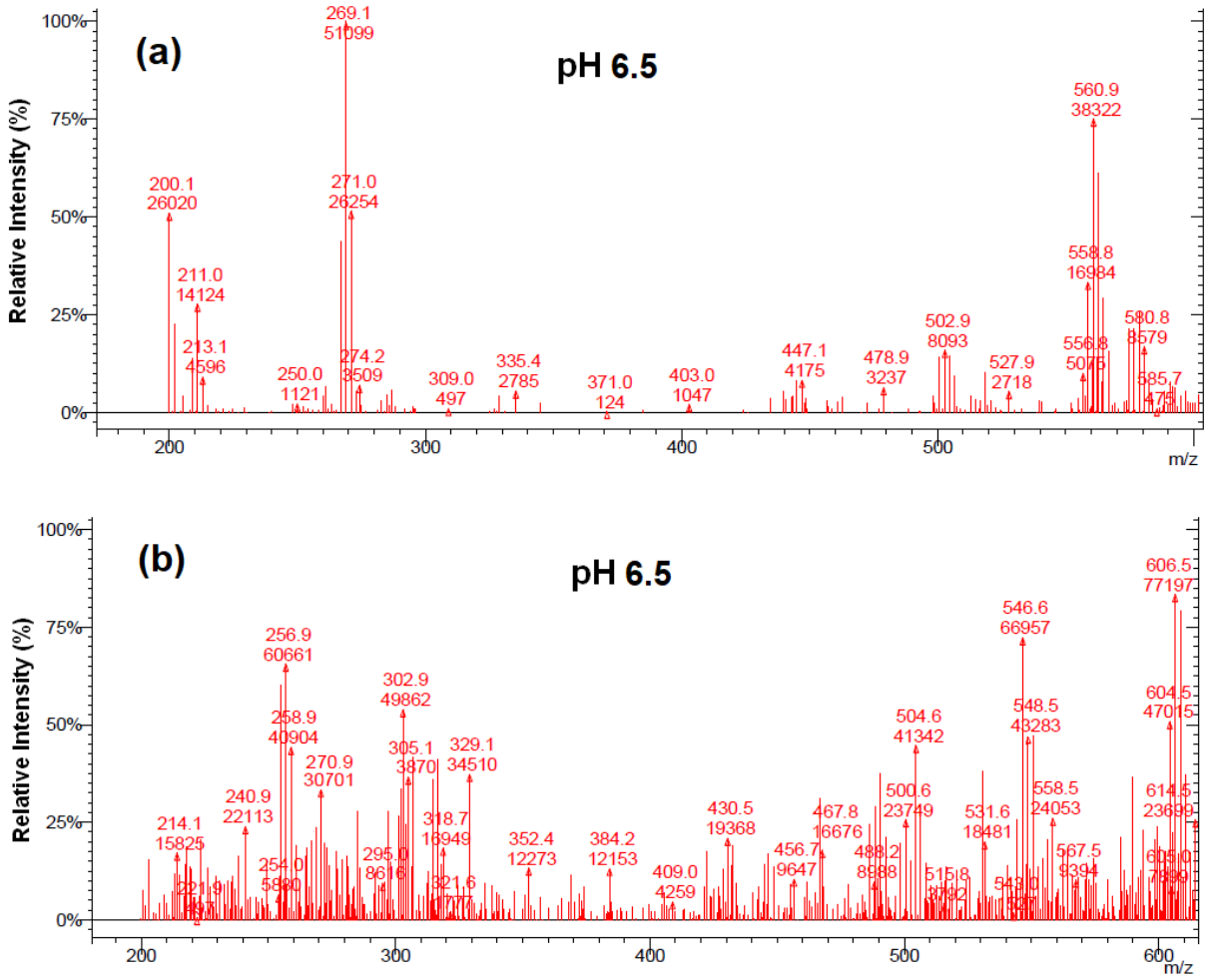


**Fig. S5. (a)** Negative-ion ESI–MS spectrum for the complexes formed in the $FeCl_3$/PicHA system at ligand-to-metal molar ratio 4:1, pH 6.5, $C_{Fe(III)} = 2.5 \times 10^{-4}$ mol $L^{-1}$.

**(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]$^+$.

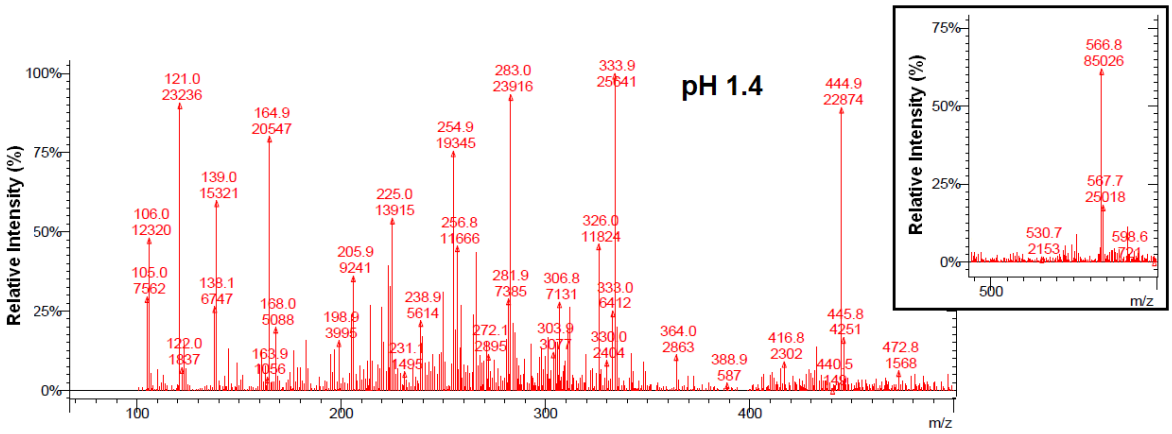


**Fig. S6.** Positive-ion ESI–MS spectrum for the complexes formed in the $VOSO_4$/PicHA system at ligand-to-metal molar ratio 2:1, pH 1.4, $C_{VO(IV)} = 2.5 \times 10^{-3}$ mol $L^{-1}$. Explanation of the signals described in the text:

*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 $[(VO)_2L_2 + SO_4 + NaOH + Na]^+$.

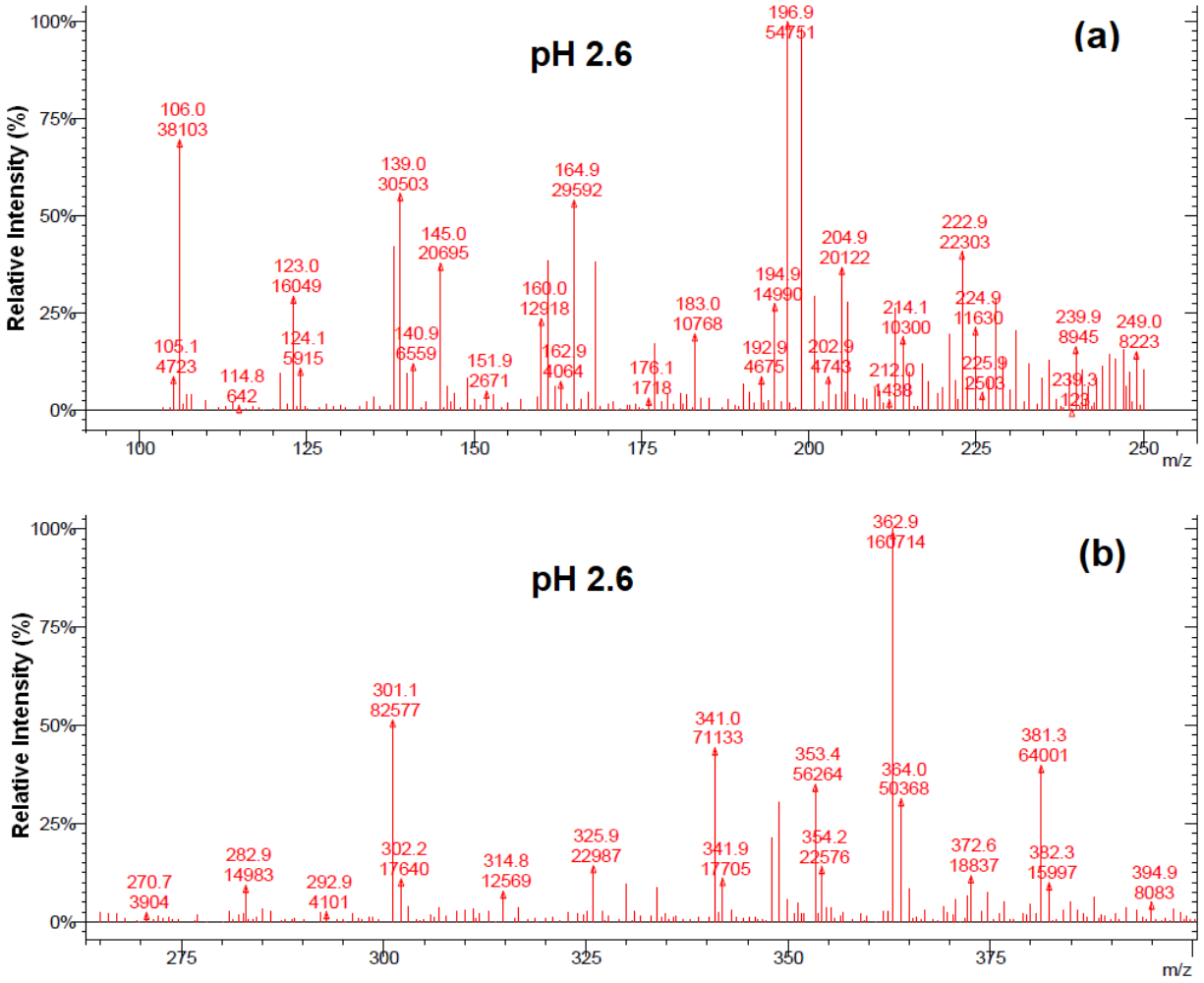


**Fig. S7.** Positive-ion ESI–MS spectrum for the complexes formed in the $VOSO_4$/PicHA system at ligand-to-metal molar ratio 2:1, pH 2.6, $C_{VO(IV)} = 2.5 \times 10^{-3}$ mol $L^{-1}$.