

**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 3. **Fig. S1. (a)** UV-Vis spectra of iron(III) chloride within the pH range 0.91 – 5.73, $C_{\text{FeCl}_3} = 5.0 \times 10^{-4} \text{ mol L}^{-1}$. **(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.

Page 4. **Fig. S2.** Tandem mass spectrum of $[\text{LH}_2]^+ - m/z = 139.0$, $C_{\text{PicHA}} = 1.0 \times 10^{-2} \text{ mol L}^{-1}$.

Page 4. **Fig. S3.** Negative-ion ESI–MS spectrum for the complexes formed in the $\text{FeCl}_3/\text{PicHA}$ system at ligand-to-metal molar ratio 4:1, pH 1.6, $C_{\text{Fe(III)}} = 2.5 \times 10^{-4} \text{ mol L}^{-1}$. Explanation of the signal described in the text:
 $m/z = 256.0 [\text{Fe(III)} + \text{fragment ion } m/z = 78 + 3\text{Cl} + \text{OH}]^-$.

Page 5. **Fig. S4. (a)** Negative-ion ESI–MS spectrum for the complexes formed in the $\text{FeCl}_3/\text{PicHA}$ system at ligand-to-metal molar ratio 4:1, pH 3.2, $C_{\text{Fe(III)}} = 2.5 \times 10^{-4} \text{ mol L}^{-1}$. Explanation of the signal described in the text:

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

(b) Positive-ion ESI–MS spectrum for the complexes formed in the $\text{FeCl}_3/\text{PicHA}$ system at ligand-to-metal molar ratio 4:1, pH 3.2, $C_{\text{Fe(III)}} = 2.5 \times 10^{-4} \text{ mol L}^{-1}$. Explanation of the signals described in the text:

$m/z = 197.0 [\text{Fe(II)} + \text{fragment ion } m/z = 106 + \text{Cl}]^+$

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

Page 6. **Fig. S5. (a)** Negative-ion ESI–MS spectrum for the complexes formed in the FeCl₃/PicHA system at ligand-to-metal molar ratio 4:1, pH 6.5, $C_{\text{Fe(III)}} = 2.5 \times 10^{-4} \text{ mol L}^{-1}$.

(b) Positive-ion ESI–MS spectrum for the complexes formed in the FeCl₃/PicHA system at ligand-to-metal molar ratio 4:1, pH 6.5, $C_{\text{Fe(III)}} = 2.5 \times 10^{-4} \text{ mol L}^{-1}$. Explanation of the signal described in the text:
 $m/z = 303.0 [\text{Fe(II)} + 2\text{fragment ions } m/z = 106 + \text{Cl}]^+$.

Page 7. **Fig. S6.** Positive-ion ESI–MS spectrum for the complexes formed in the VOSO₄/PicHA system at ligand-to-metal molar ratio 2:1, pH 1.4, $C_{\text{VO(IV)}} = 2.5 \times 10^{-3} \text{ mol L}^{-1}$. Explanation of the signals described in the text:

$m/z = 282.0 [\text{VOL} + \text{fragment ion } m/z = 78]^+$

$m/z = 283.0 [\text{L} + \text{fragment ion } m/z = 122 + \text{Na} + \text{H}]^+$

$m/z = 326.0 [\text{VOL} + \text{fragment ion } m/z = 122]^+$

$m/z = 567.0 [(\text{VO})_2\text{L}_2 + \text{SO}_4 + \text{NaOH} + \text{Na}]^+$.

Page 8. **Fig. S7** Positive-ion ESI–MS spectrum for the complexes formed in the VOSO₄/PicHA system at ligand-to-metal molar ratio 2:1, pH 2.6, $C_{\text{VO(IV)}} = 2.5 \times 10^{-3} \text{ mol L}^{-1}$.

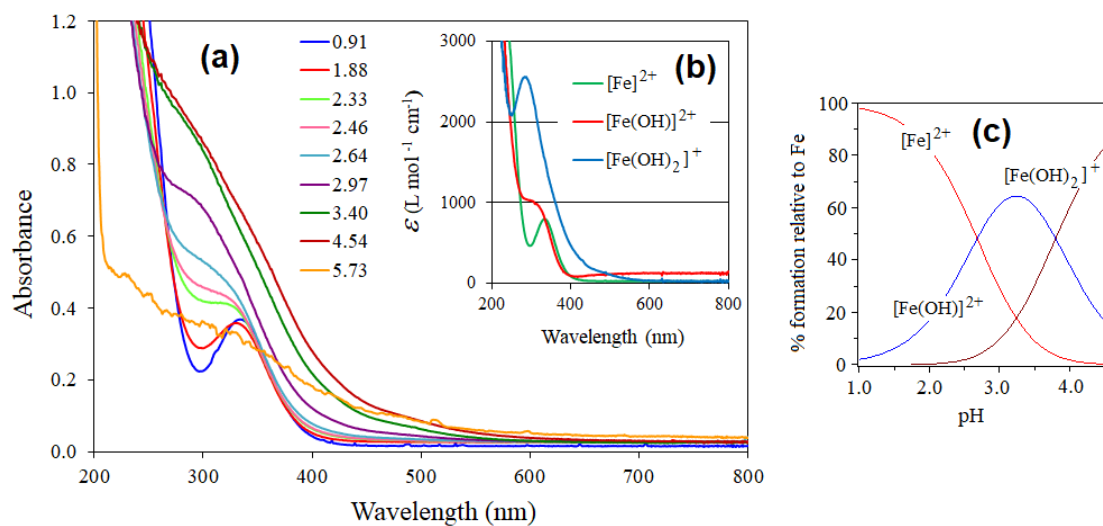


Fig. S1. (a) UV-Vis spectra of iron(III) chloride within the pH range 0.91 – 5.73, $C_{\text{FeCl}_3} = 5.0 \times 10^{-4} \text{ mol L}^{-1}$. **(b)** Molar absorption coefficients for various Fe(III) aqua-hydroxo complexes. **(c)** Species distribution curves as a function of pH for the Fe(III) aqua-hydroxo complexes.

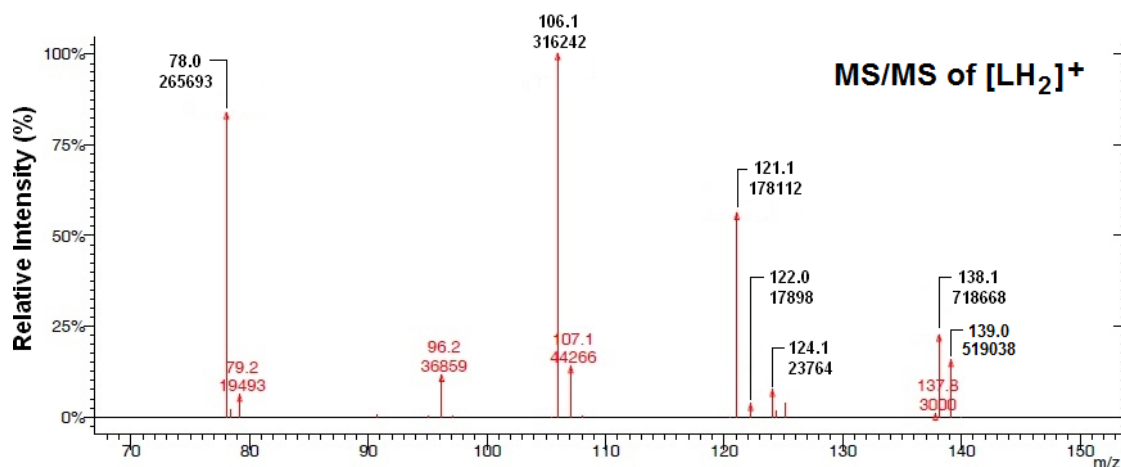


Fig. S2. Tandem mass spectrum of [LH₂]⁺ – $m/z = 139.0$, $C_{\text{PicHA}} = 1.0 \times 10^{-2} \text{ mol L}^{-1}$.

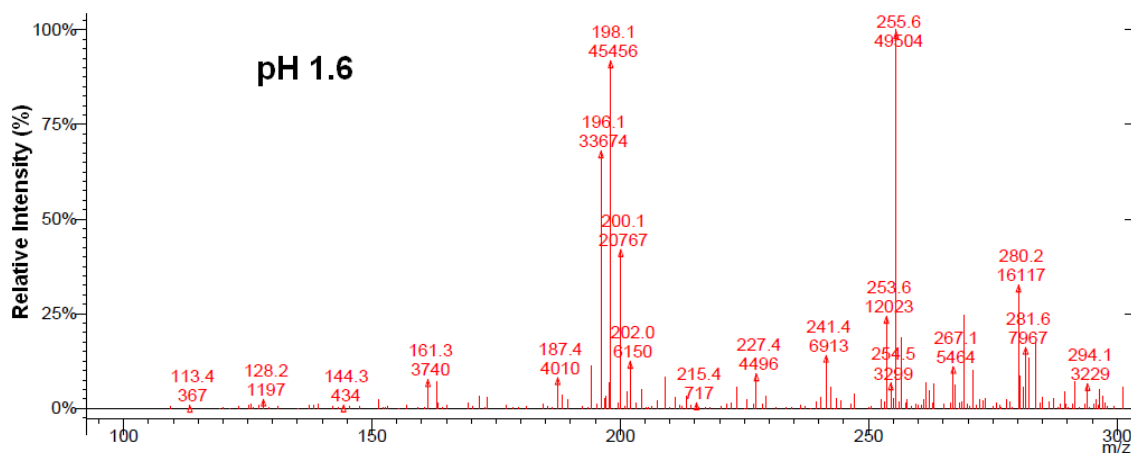


Fig. S3. Negative-ion ESI–MS spectrum for the complexes formed in the FeCl₃/PicHA system at ligand-to-metal molar ratio 4:1, pH 1.6, $C_{\text{Fe(III)}} = 2.5 \times 10^{-4} \text{ mol L}^{-1}$.

Explanation of the signal described in the text:

$m/z = 256.0$ [Fe(III) + fragment ion $m/z = 78 + 3\text{Cl} + \text{OH}$][−].

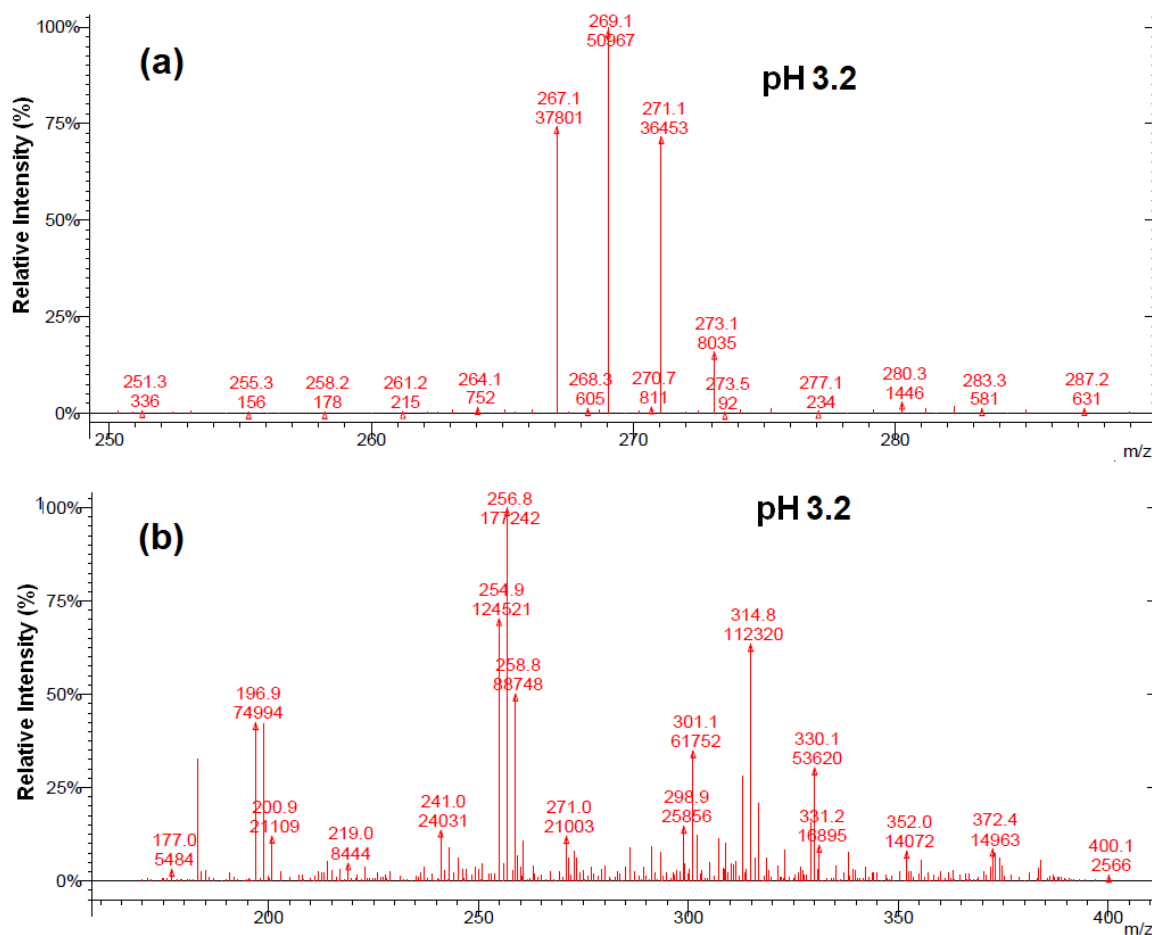


Fig. S4. (a) Negative-ion ESI–MS spectrum for the complexes formed in the $\text{FeCl}_3/\text{PicHA}$ system at ligand-to-metal molar ratio 4:1, pH 3.2, $C_{\text{Fe(III)}} = 2.5 \times 10^{-4} \text{ mol L}^{-1}$. Explanation of the signal described in the text:

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

(b) Positive-ion ESI–MS spectrum for the complexes formed in the $\text{FeCl}_3/\text{PicHA}$ system at ligand-to-metal molar ratio 4:1, pH 3.2, $C_{\text{Fe(III)}} = 2.5 \times 10^{-4} \text{ mol L}^{-1}$. Explanation of the signals described in the text:

$m/z = 197.0$ $[\text{Fe(II)} + \text{fragment ion } m/z = 106 + \text{Cl}]^+$

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

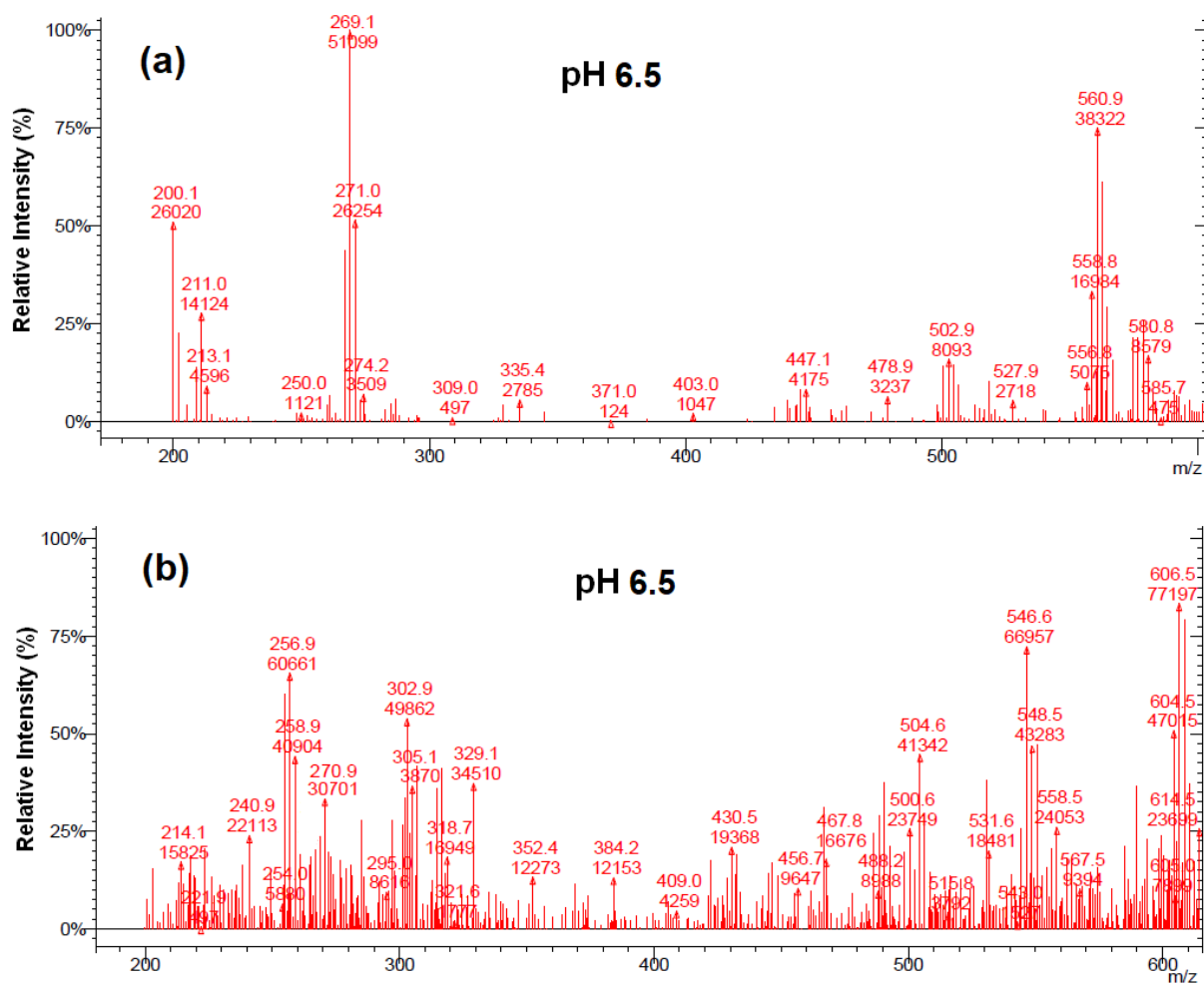


Fig. S5. (a) Negative-ion ESI–MS spectrum for the complexes formed in the $\text{FeCl}_3/\text{PicHA}$ system at ligand-to-metal molar ratio 4:1, pH 6.5, $C_{\text{Fe(III)}} = 2.5 \times 10^{-4} \text{ mol L}^{-1}$.

(b) Positive-ion ESI–MS spectrum for the complexes formed in the $\text{FeCl}_3/\text{PicHA}$ system at ligand-to-metal molar ratio 4:1, pH 6.5, $C_{\text{Fe(III)}} = 2.5 \times 10^{-4} \text{ mol L}^{-1}$.
Explanation of the signal described in the text:



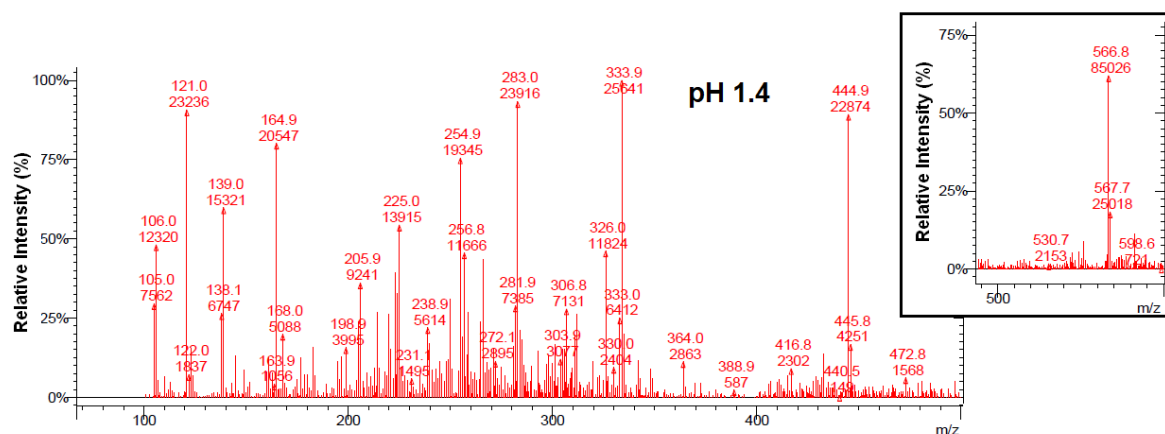


Fig. S6. Positive-ion ESI-MS spectrum for the complexes formed in the $\text{VOSO}_4/\text{PicHA}$ system at ligand-to-metal molar ratio 2:1, pH 1.4, $C_{\text{VO(IV)}} = 2.5 \times 10^{-3} \text{ mol L}^{-1}$. Explanation of the signals described in the text:

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

$m/z = 283.0$ [L + fragment ion $m/z = 122 + \text{Na} + \text{H}$]⁺

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

$m/z = 567.0$ [(VO)₂L₂ + SO₄ + NaOH + Na]⁺.

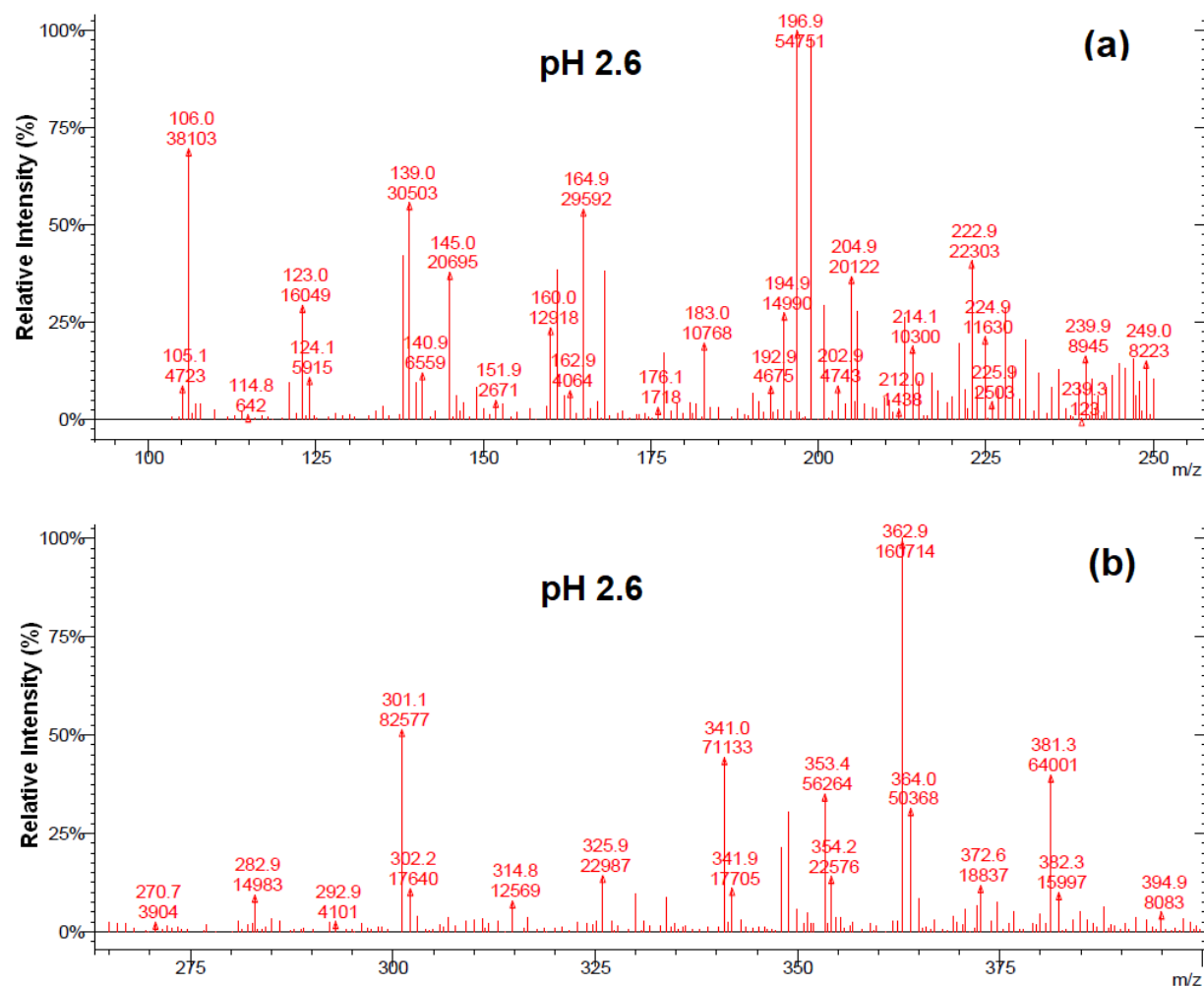


Fig. S7. Positive-ion ESI-MS spectrum for the complexes formed in the $\text{VOSO}_4/\text{PicHA}$ system at ligand-to-metal molar ratio 2:1, pH 2.6, $C_{\text{VO(IV)}} = 2.5 \times 10^{-3} \text{ mol L}^{-1}$.