

Supplementary Information for the paper

## The peculiar behavior of Picha in the formation of metallacrown complexes with Cu(II), Ni(II) and Zn(II), in aqueous solution

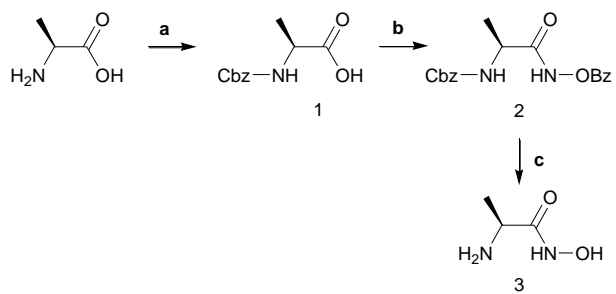
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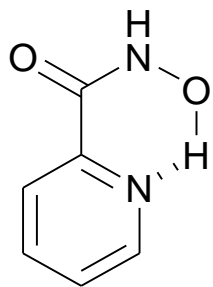
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**Table S1.** Logarithms of protonation and Ni(II) complex formation constants of the complexes with Picha, obtained by treating the potentiometric data with inclusion of the 12-MC-4 species in the speciation model.  $T = 298.2 \text{ K}$ ,  $I = 0.1 \text{ mol L}^{-1}$  (KCl)

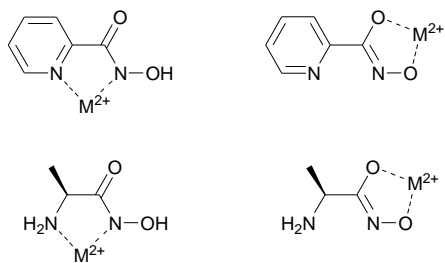
Species <sup>[a]</sup>	Picha (HL)
[NiL] <sup>+</sup>	7.16(1)
[NiL <sub>2</sub> ]	13.95(1)
[NiL <sub>3</sub> ] <sup>-</sup>	19.39(2)
[NiL(LH <sub>1</sub> )] <sup>-</sup>	4.24(3)
[Ni <sub>5</sub> (LH <sub>1</sub> ) <sub>4</sub> ] <sup>2+</sup>	15.77(9)
[Ni <sub>5</sub> (LH <sub>1</sub> ) <sub>5</sub> ]	13.96(13)
$\sigma; n$	1.31; 207



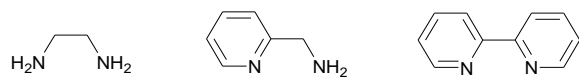
**Scheme S1.** Synthesis of Alaha (**3**). (a) CbzCl, NaOH (aq). (b) Ethylchloroformate, *N*-methylmorpholine, dichloromethane. (c) H<sub>2(g)</sub>, Pd/C (10 %).



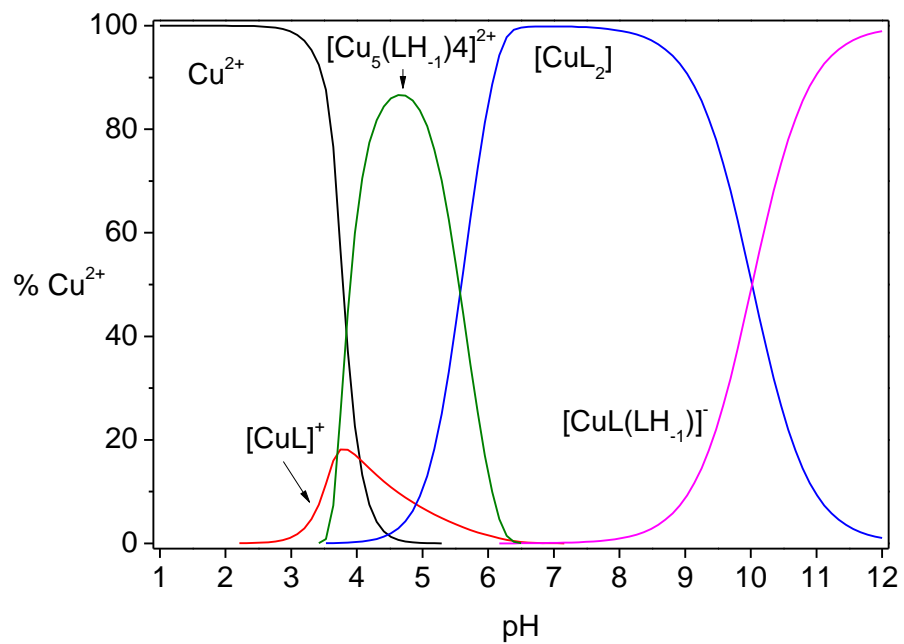
**Scheme S2.** Scheme of Pictin and potential intramolecular hydrogen bond.



**Scheme S3.** Representation of the possible ( $N,N$ ) and ( $O,O$ ) coordination modes for Picha (above) and Alaha (below).

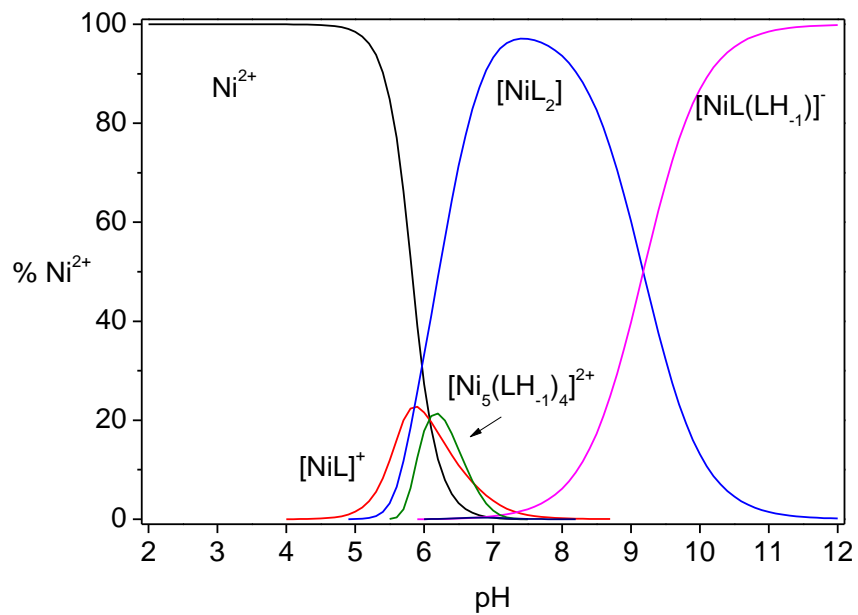


**Scheme S4.** Schematic drawings of the ligands ethylenediamine (en, left), picolinamine (Pyam, center) and 2,2'-bipyridine (Bipy, right).

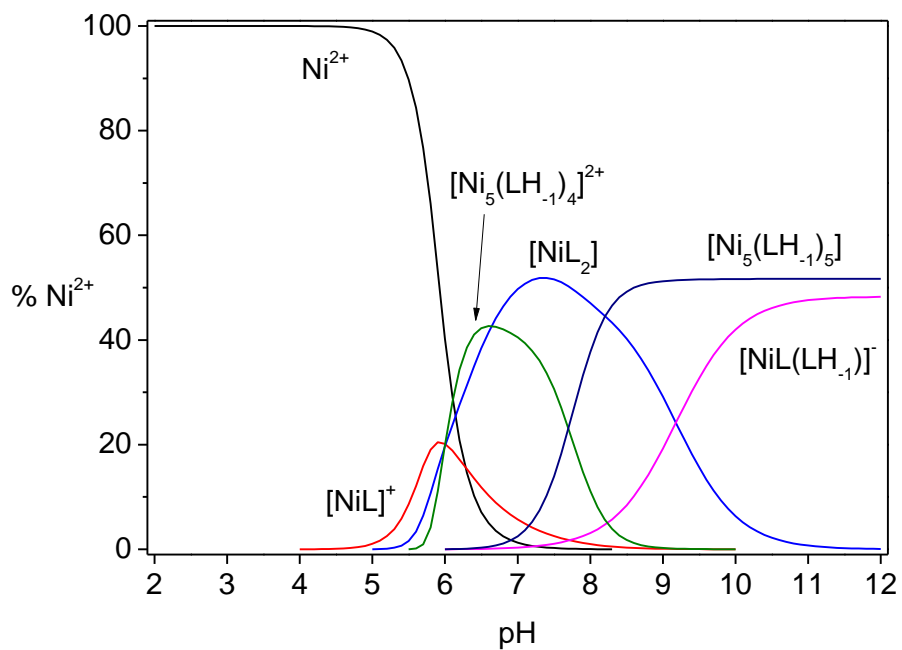


**Figure S1.** Representative speciation diagram of the system Cu(II) / Alaha (HL). Cu:L = 1:2.2,  $C_{\text{Cu}} = 2.8 \times 10^{-3}$  mol L<sup>-1</sup>,  $I = 0.1$  mol L<sup>-1</sup> (KCl),  $T = 298.2$  K.

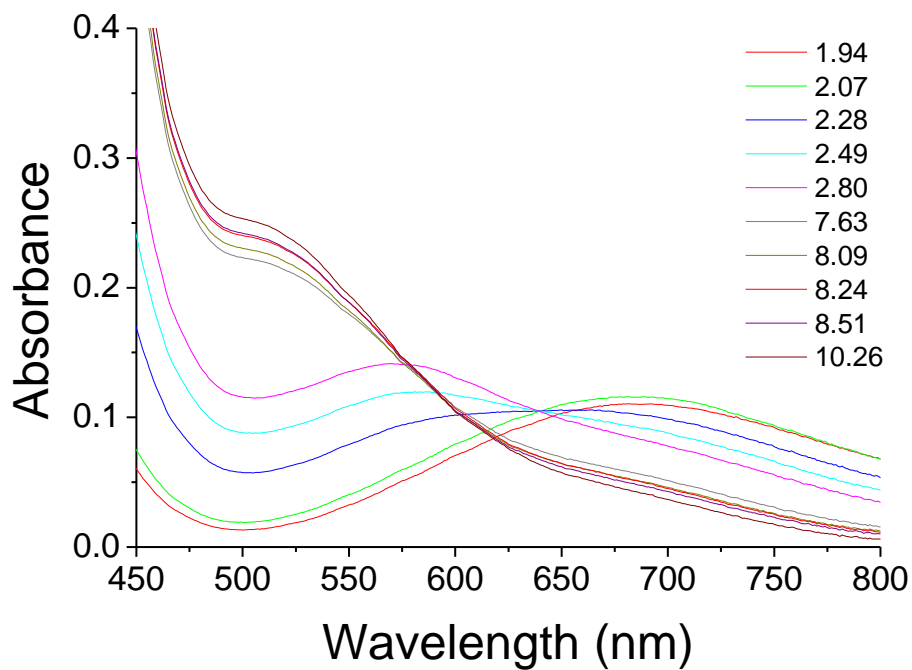




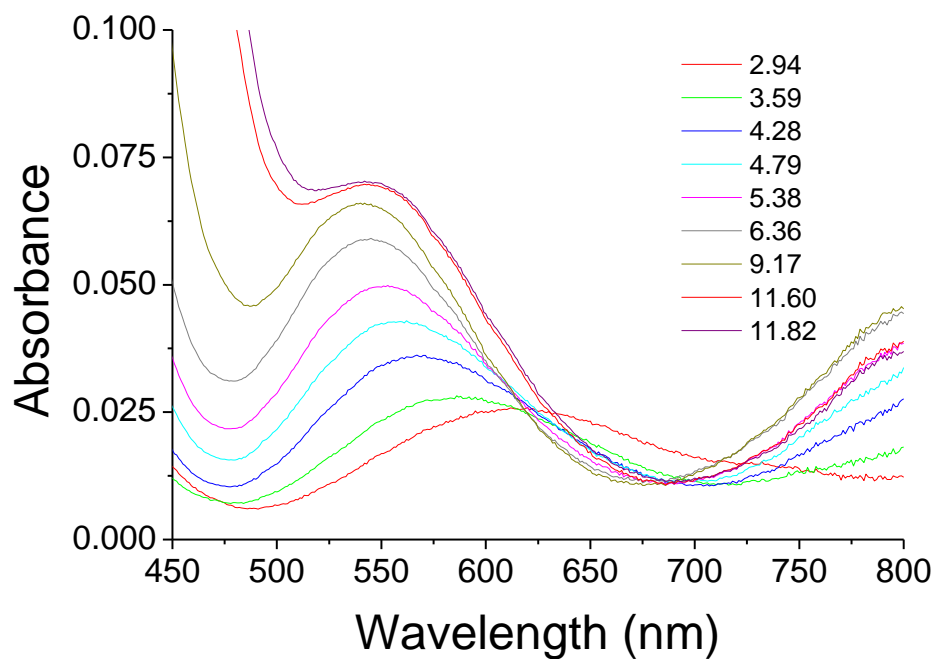
**Figure S2.** Representative speciation diagram of the system Ni(II) / Alaha (HL). Ni:L = 1:2.2,  $C_{\text{Ni}} = 2.8 \times 10^{-3} \text{ mol L}^{-1}$ ,  $I = 0.1 \text{ mol L}^{-1}$  (KCl),  $T = 298.2 \text{ K}$ .



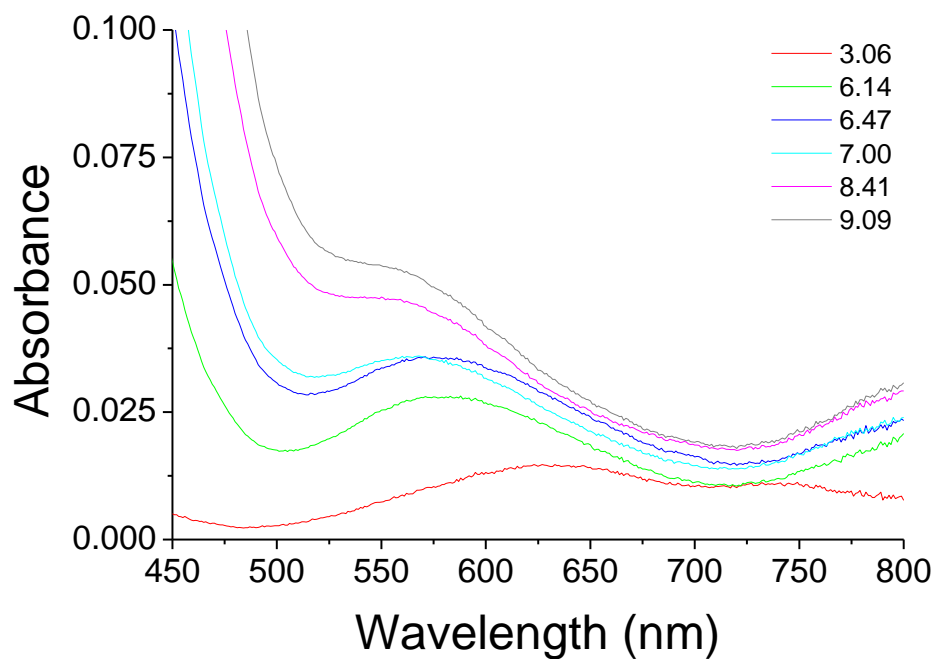
**Figure S3.** Representative speciation diagram of the system Ni(II) / Alaha (HL). Ni:L = 1:1.5,  $C_{\text{Ni}} = 2.8 \times 10^{-3} \text{ mol L}^{-1}$ ,  $I = 0.1 \text{ mol L}^{-1}$  (KCl),  $T = 298.2 \text{ K}$ .



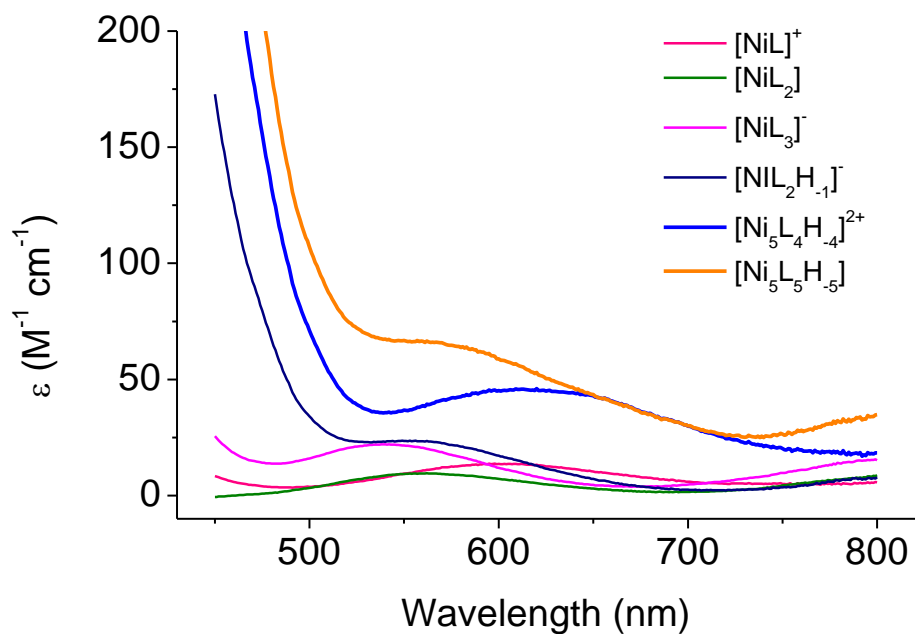
**Figure S4.** Experimental visible spectra for the system Cu(II) / Picha 1:2.17 ( $C_{\text{Cu}} = 2.31 \times 10^{-3} \text{ mol L}^{-1}$ ,  $I = 0.1 \text{ M KCl}$ ) at different pH (see values in the inset).



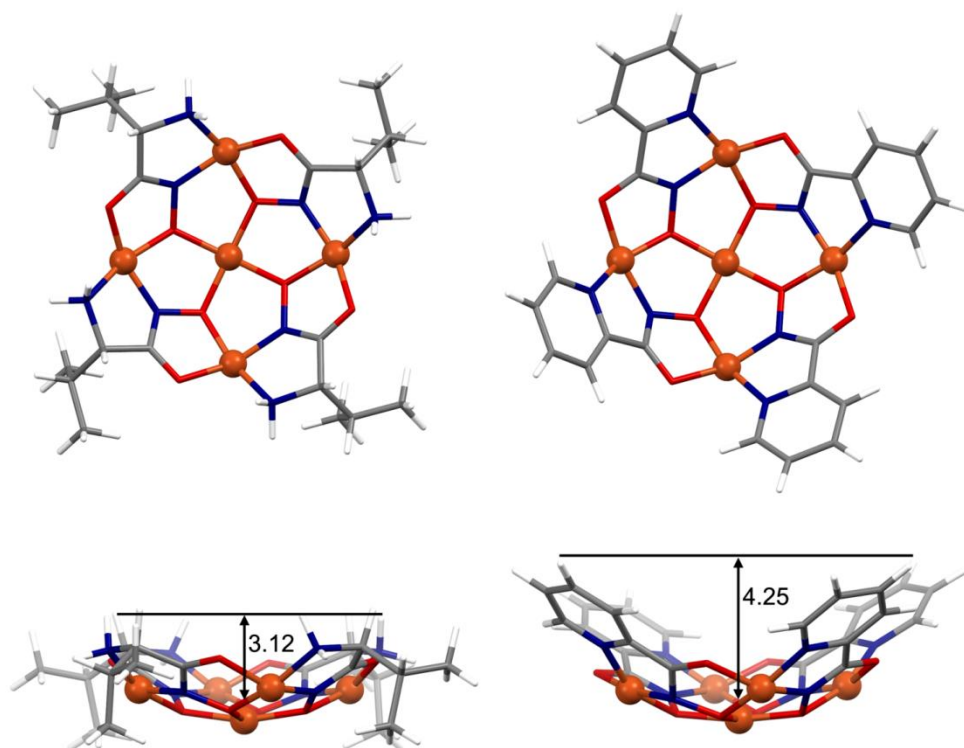
**Figure S5.** Experimental visible spectra for the system Ni(II) / Picha 1:2.73 ( $C_{\text{Ni}} = 3.67 \times 10^{-3} \text{ mol L}^{-1}$ ,  $I = 0.1 \text{ M KCl}$ ) at different pH (see values in the inset).



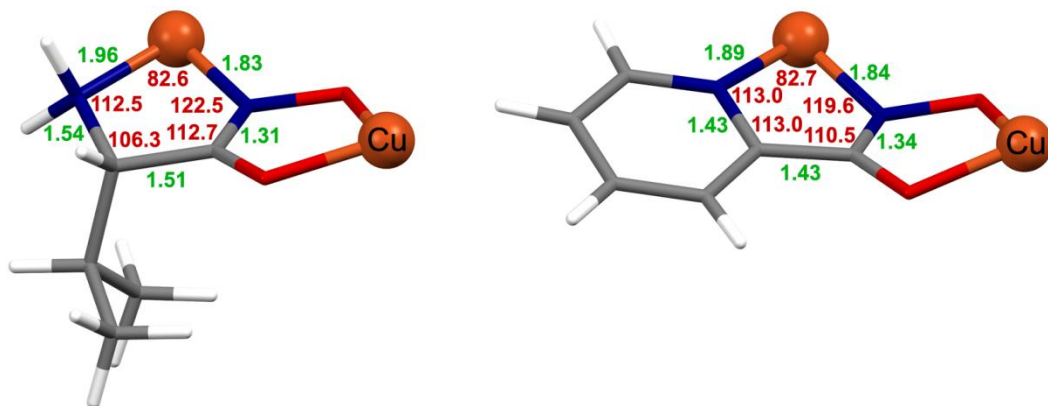
**Figure S6.** Experimental visible spectra for the system Ni(II) / Picha 1:1.45 ( $C_{\text{Ni}} = 3.67 \times 10^{-3} \text{ mol L}^{-1}$ ,  $I = 0.1 \text{ M KCl}$ ) at different pH (see values in the inset).



**Figure S7.** Calculated molar visible spectra for the complex species in the Ni(II) / Picha (HL) system, after the treatment with a speciation model which includes the 12-MC-4 complex.  $I = 0.1 \text{ mol L}^{-1}$  (KCl),  $T = 298.2 \text{ K}$ .



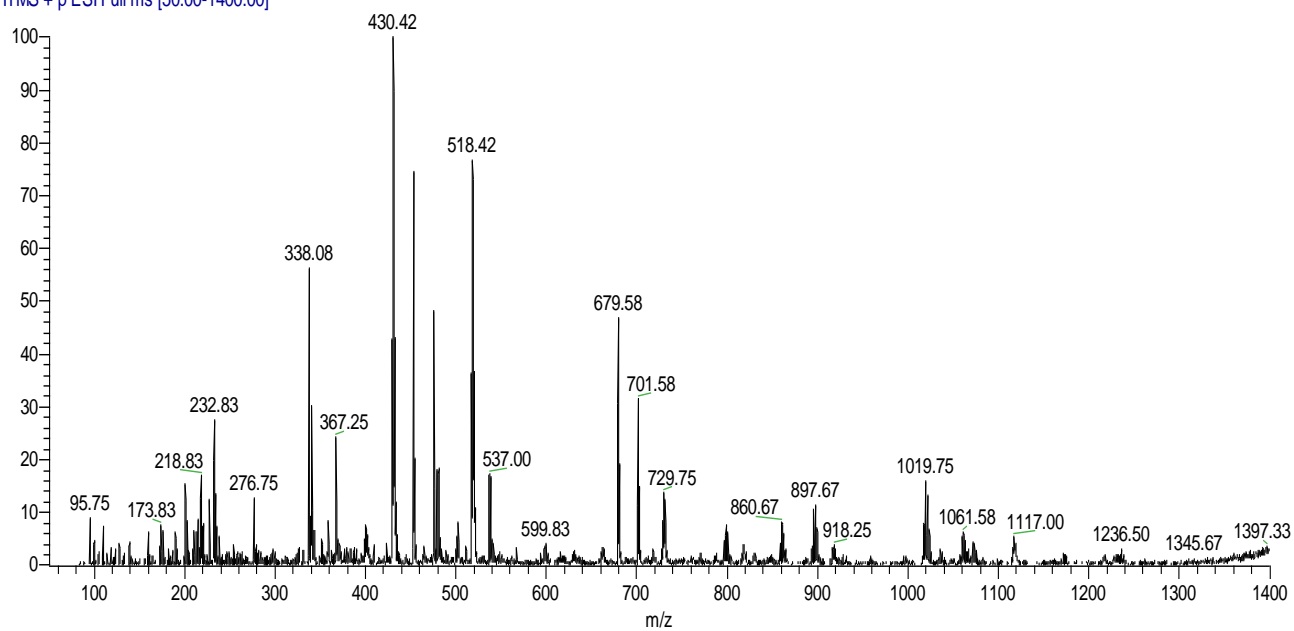
**Figure S8.** Comparison between of the optimized molecular structures (B3LYP/3-21G) of the 12-MC-4  $[Cu_5(LH_1)_4]^{2+}$  with HL = valinehydroxamic acid (Valha) (left) and HL = Picha (right).



**Figure S9.** Comparison between the geometry of the valinehydroxamate (Valha) ligand (left) and of the ligand Picha (right) in the optimized structures of the respective 12-MC-4  $[\text{Cu}_5(\text{LH}_1)_4]^{2+}$ . Bond distances (Å) in green and bond angles (°) in red.

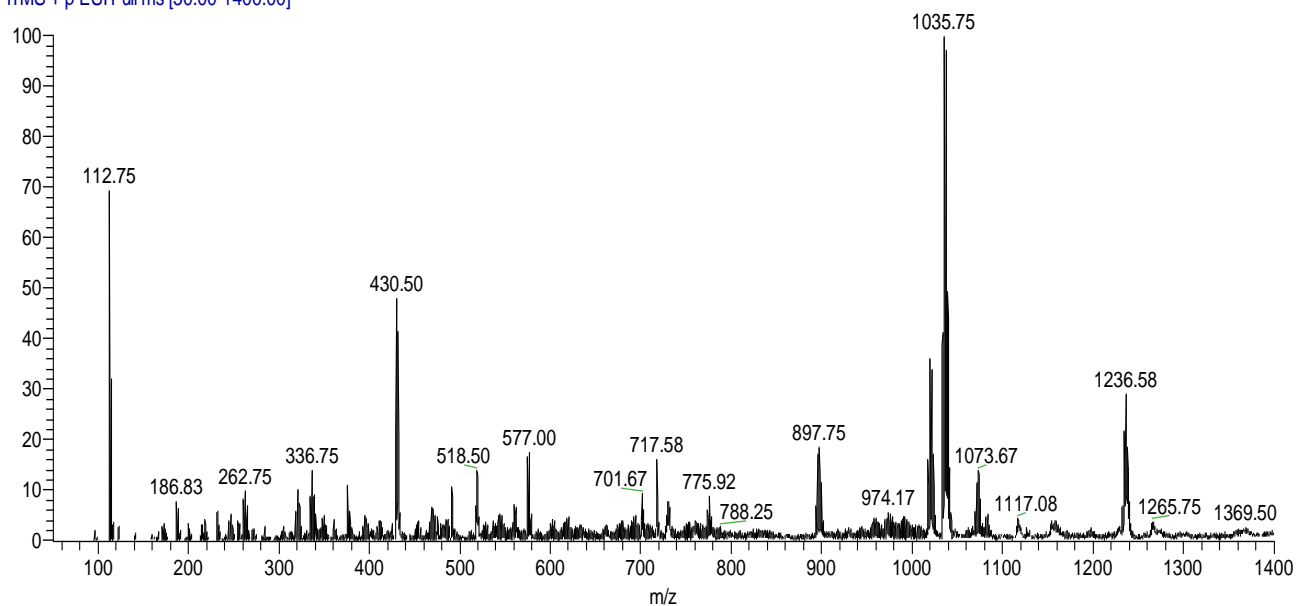


CuAHA\_004 #1 RT: 0.00 AV: 1 NL: 6.66E3  
T: ITMS + p ESI Full ms [50.00-1400.00]



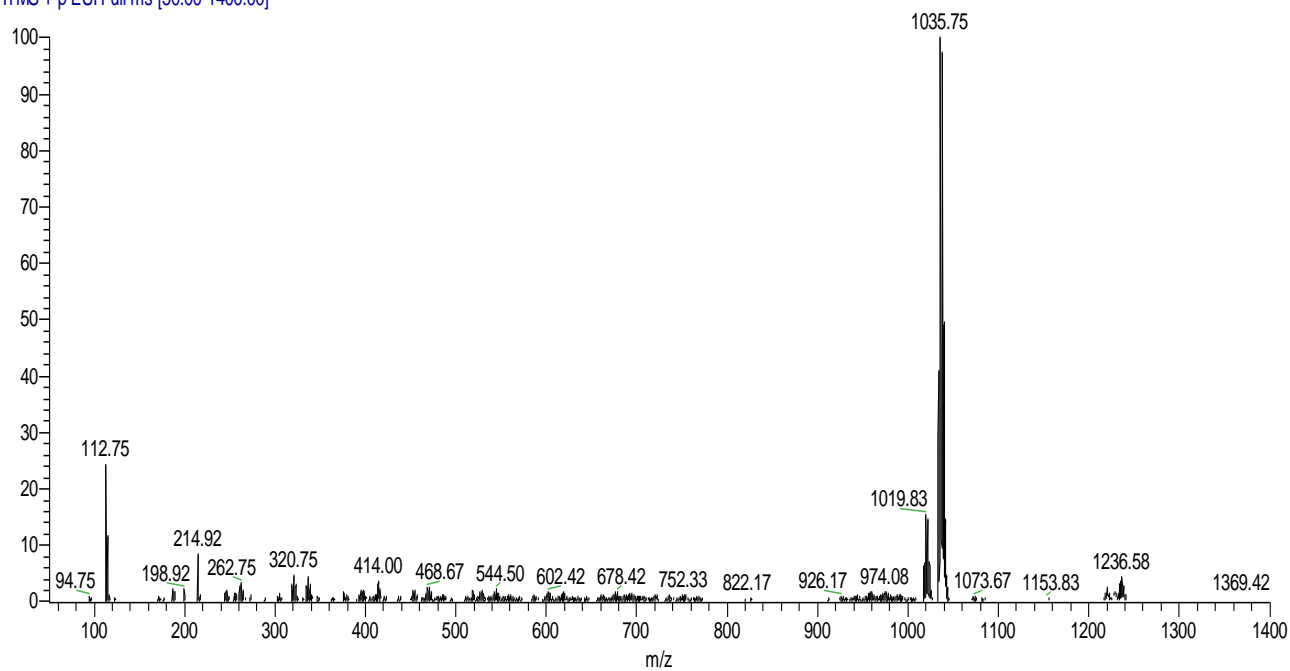
**Figure S10.** Positive ion ESI-MS spectrum for the complex of the system Cu(II)/PicHA 5:6 mM in aqueous solution, pH = 2.3.

picAHA\_008 #1 RT: 0.00 AV: 1 NL: 3.14E4  
T: ITMS + p ESI Full ms [50.00-1400.00]



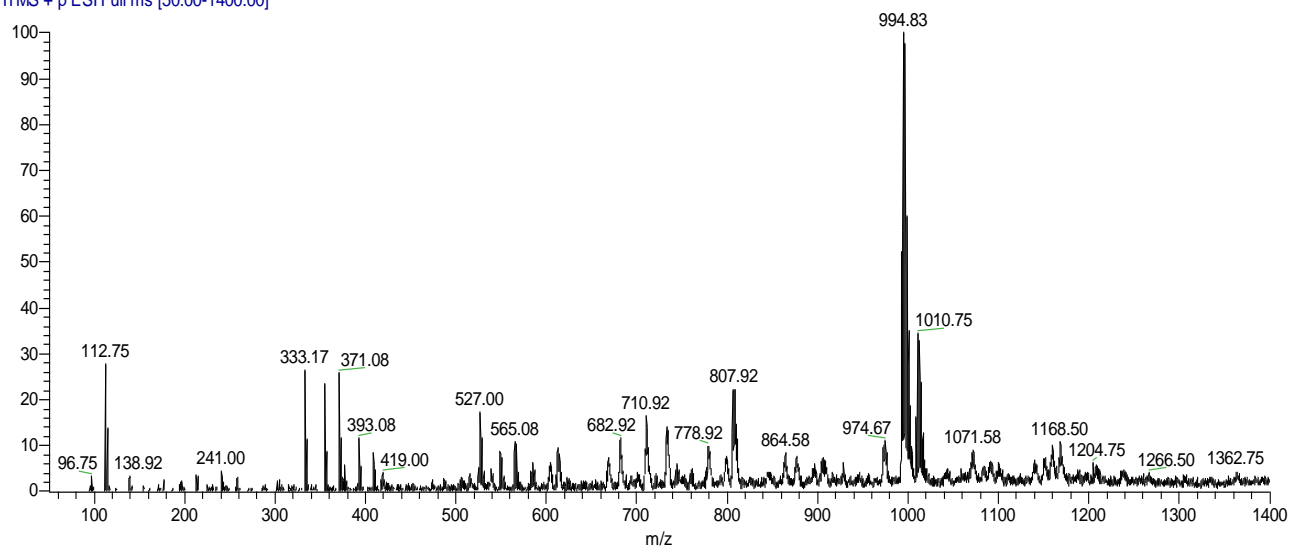
**Figure S11.** Positive ion ESI-MS spectrum for the complex of the system Cu(II)/PicHA 5:6 mM in aqueous solution, pH = 6.0.

Cu\_picHA\_018 #16-386 RT: 0.04-1.13 AV: 371  
T: ITMS + p ESI Full ms [50.00-1400.00]



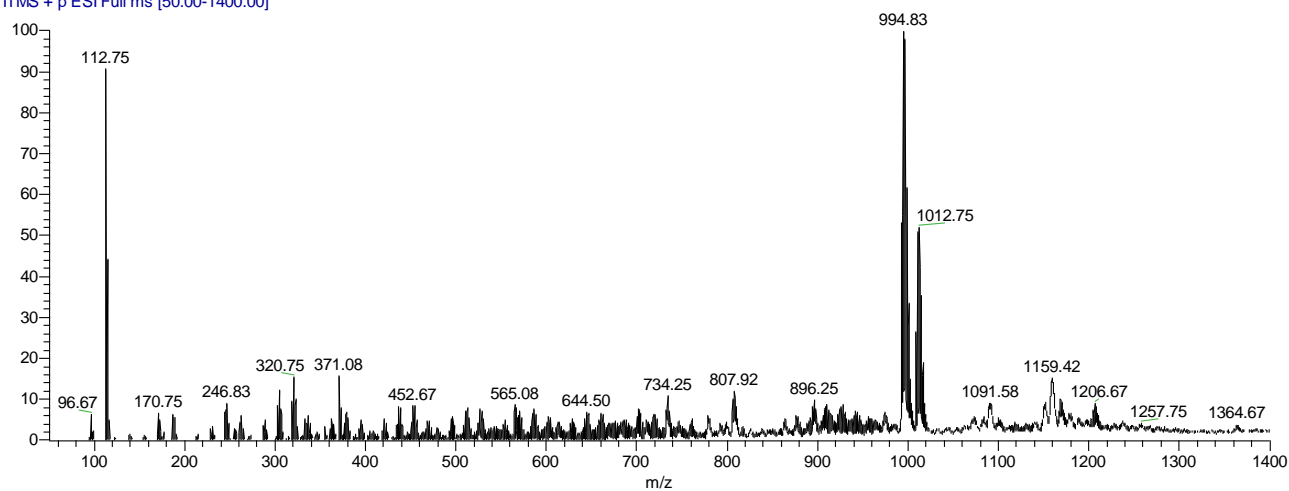
**Figure S12.** Positive ion ESI-MS spectrum for the complex of the system Cu(II)/PicHA 5:6 mM in aqueous solution, pH = 11.3.

Ni\_picHA\_011 #1 RT: 0.00 AV: 1 NL: 1.12E4  
T: ITMS + p ESI Full ms [50.00-1400.00]



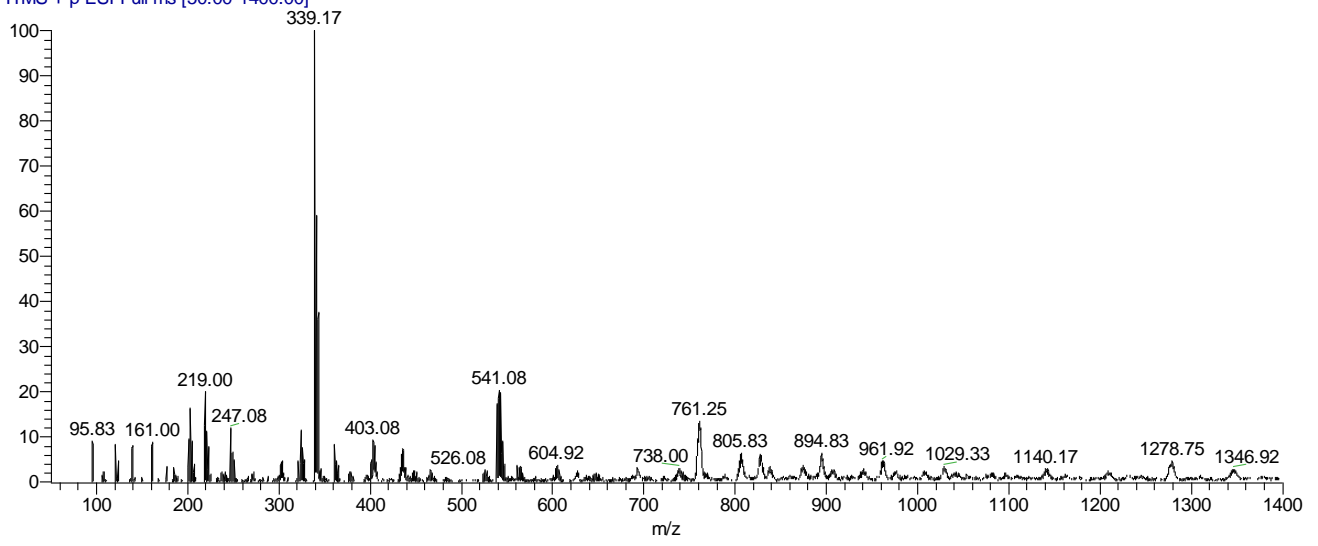
**Figure S13.** Positive ion ESI-MS spectrum for the complex of the system Ni(II)/PicHA 5:6 mM in aqueous solution, pH = 6.9.

Ni\_picHA\_023 #38-316 RT: 0.11-0.92 AV: 279  
T: ITMS + p ESI Full ms [50.00-1400.00]



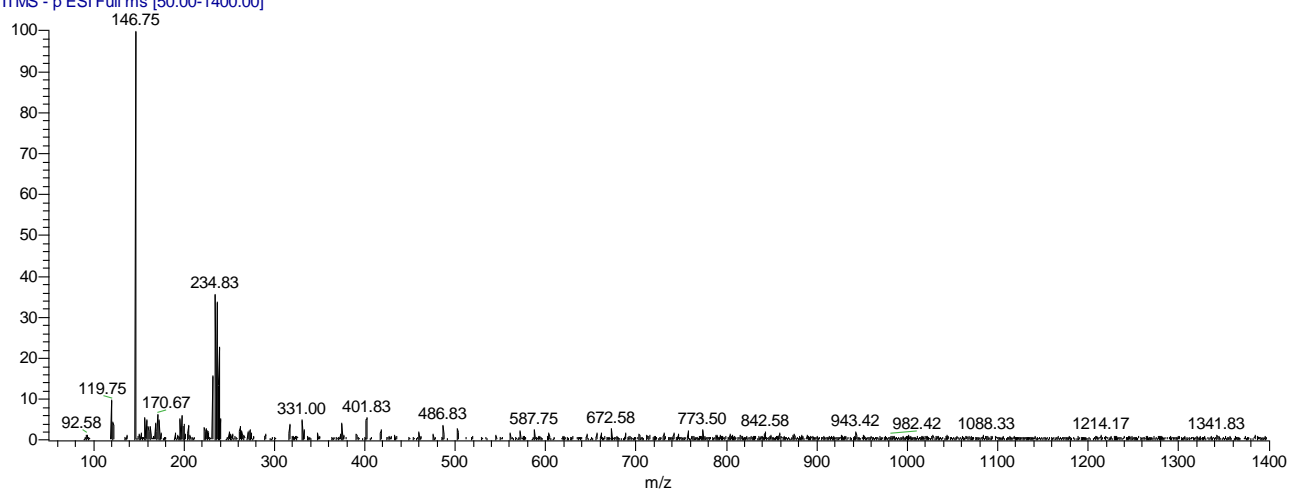
**Figure S14.** Positive ion ESI-MS spectrum for the complex of the system Ni(II)/PicHA 5:6 mM in aqueous solution, pH = 10.3.

Zi\_picHA\_014 #1 RT: 0.00 AV: 1 NL: 4.75E4  
T: ITMS + p ESI Full ms [50.00-1400.00]



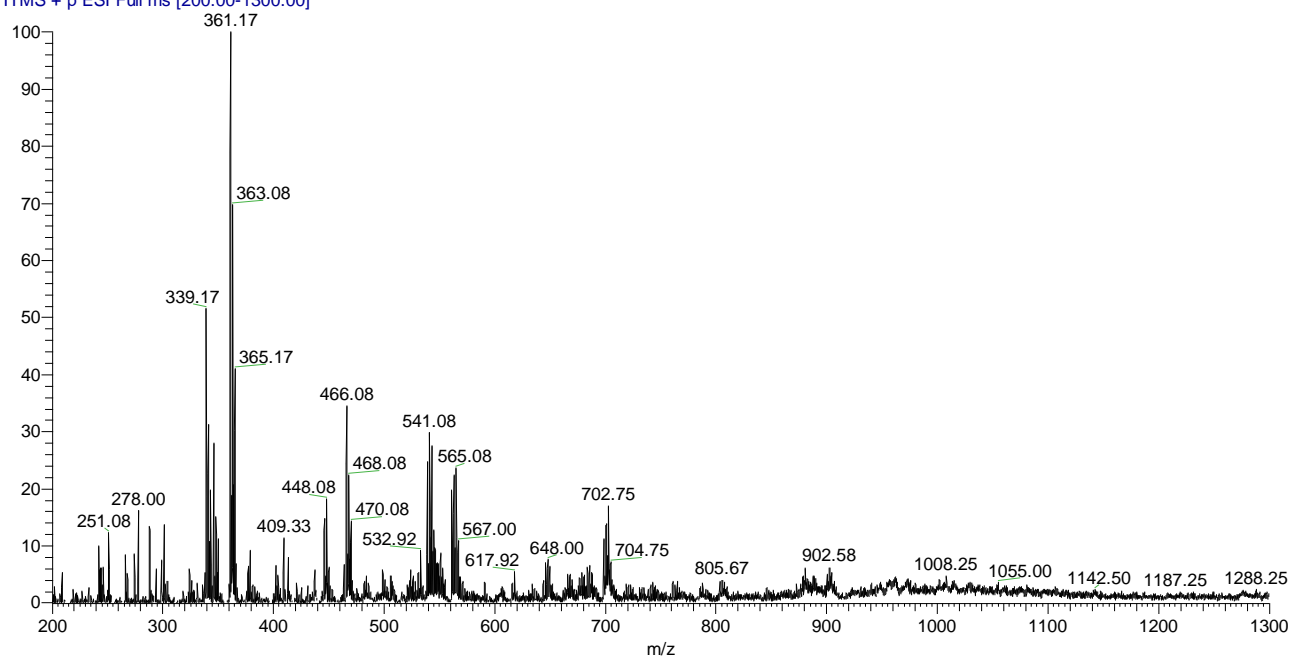
**Figure S15.** Positive-ion ESI-MS spectrum for the complex of the system Zn(II)/PicHA 5:6 mM in aqueous solution, pH = 6.0.

Zn\_picHA\_026 #1 RT: 0.00 AV: 1 NL: 3.53E3  
T: ITMS - p ESI Full ms [50.00-1400.00]



**Figure S16.** Negative-ion ESI-MS spectrum for the complex of the system Zn(II)/PicHA 5:6 mM in aqueous solution, pH = 6.0.

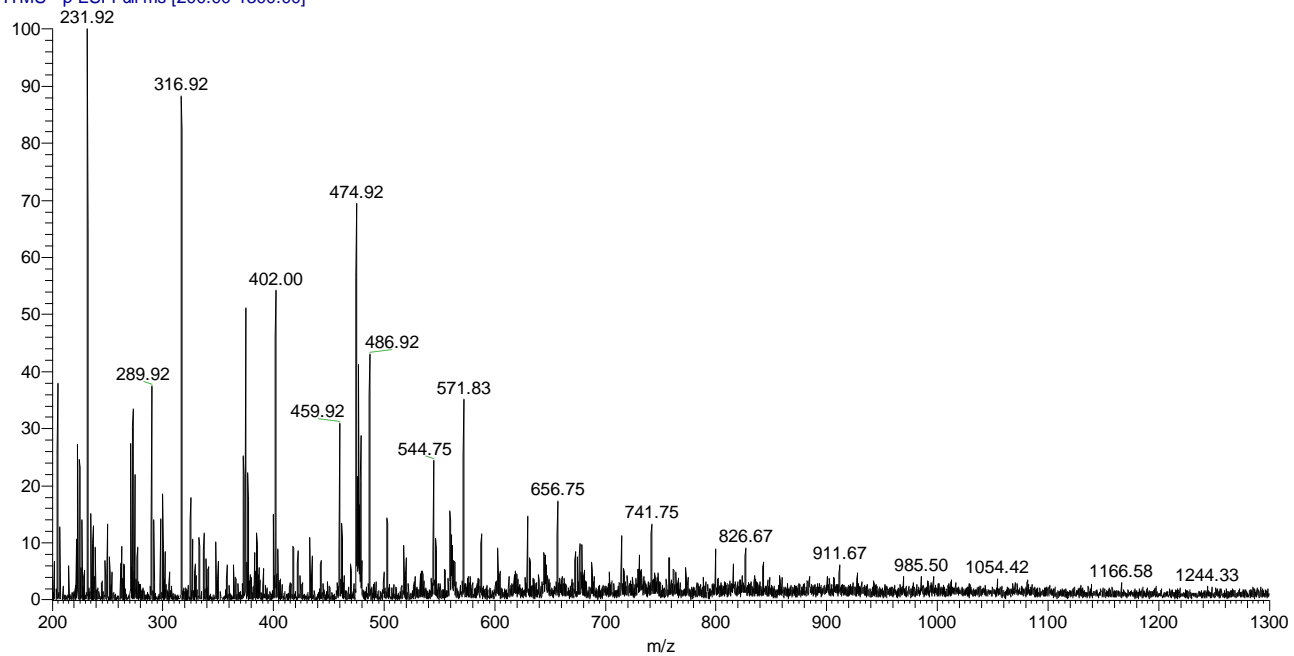
Zn\_picHA\_029 #120 RT: 0.31 AV: 1 NL: 1.30E4  
T: ITMS + p ESI Full ms [200.00-1300.00]



**Figure S17.** Positive-ion ESI-MS spectrum for the complex of the system Zn(II)/PicHA 5:8 mM in aqueous solution, pH = 7.0.

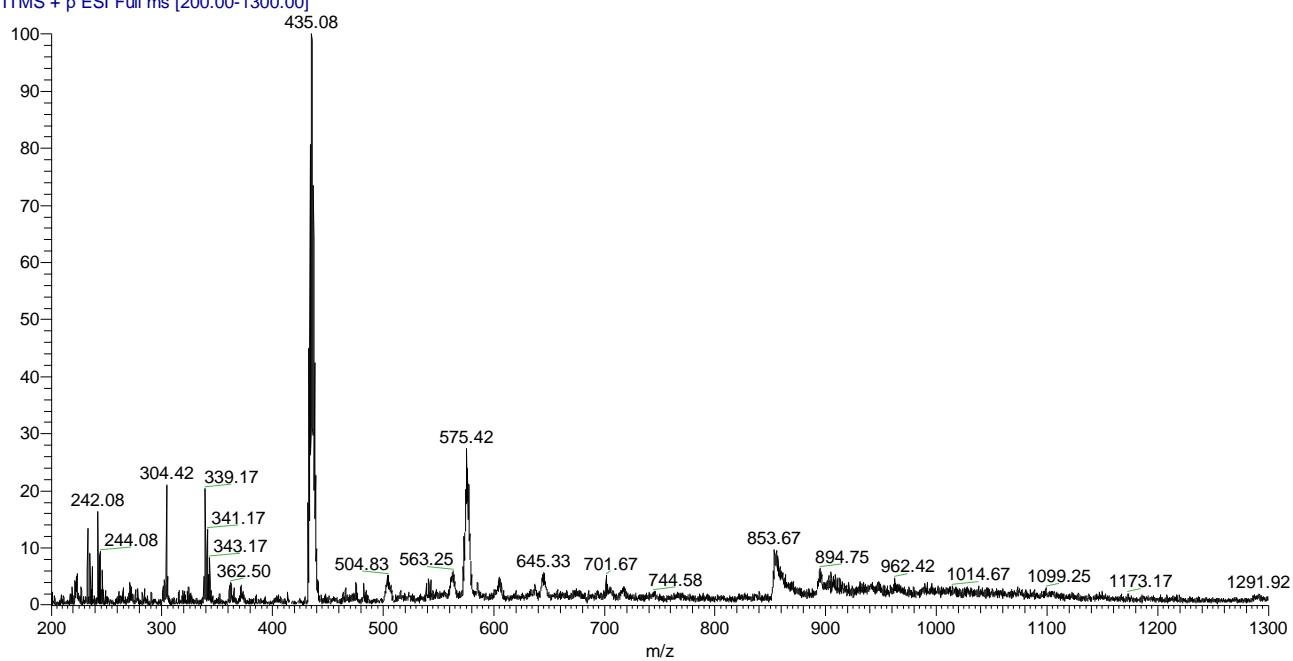


Zn\_picHA\_030 #6 RT: 0.01 AV: 1 NL: 1.71E3  
T: ITMS - p ESI Full ms [200.00-1300.00]



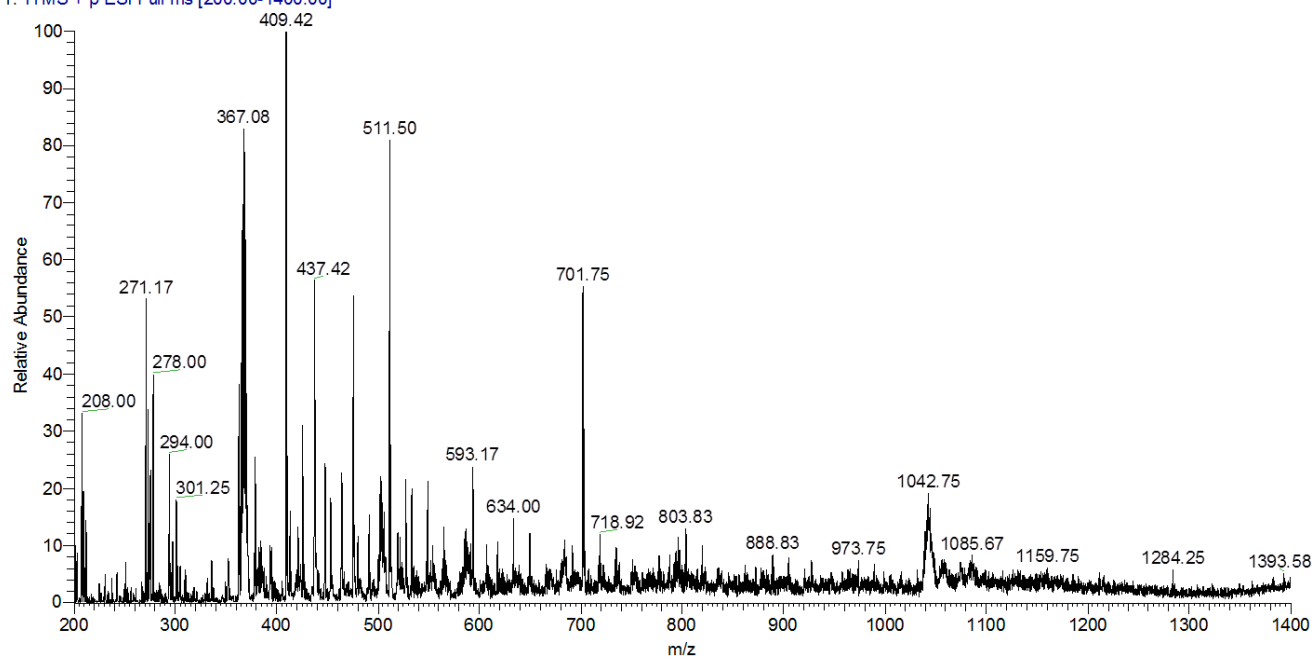
**Figure S18.** Negative-ion ESI-MS spectrum for the complex of the system Zn(II)/PicHA 5:8 mM in aqueous solution, pH = 7.0.

Zn\_picHA\_033 #1 RT: 0.00 AV: 1 NL: 1.26E4  
T: ITMS + p ESI Full ms [200.00-1300.00]



**Figure S19.** Positive-ion ESI-MS spectrum for the complex of the system Zn(II)/PicHA 8:8 mM in aqueous solution, pH = 6.3.

Zn\_alaha\_001 #1 RT: 0.00 AV: 1 NL: 3.89E3  
T: ITMS + p ESI Full ms [200.00-1400.00]



**Figure S20.** Positive-ion ESI-MS spectrum for the complex of the system Zn(II)/Alaha 5:6 mM in aqueous solution, pH = 7.2.