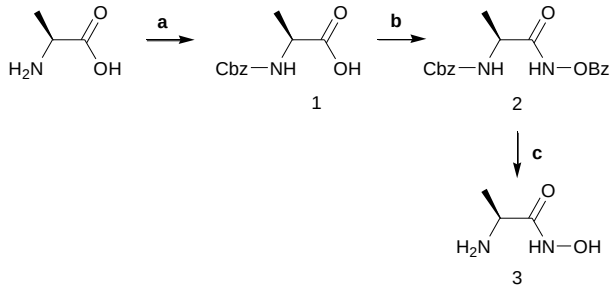
Supplementary Information for the paper

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

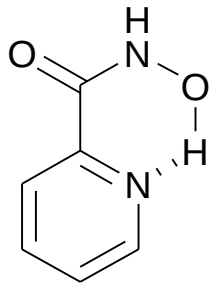
L. Marchiò,[a] N. Marchetti,[b] C. Atzeri,[a] V. Borghesani,[a] M. Remelli[b] and M. Tegoni[*a]

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 K, I = 0.1 mol L^{-1} (KCl)

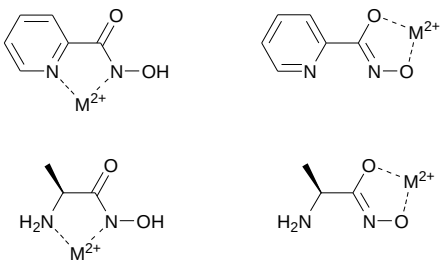
Species[a]	Picha (HL)
$[NiL]^{+}$	7.16(1)
$[NiL_2]$	13.95(1)
$[NiL_3]$-	19.39(2)
$[NiL(LH_{-1})]^{-}$	4.24(3)
$[Ni_5(LH_{-1})_4]^{2+}$	15.77(9)
$[Ni_5(LH_{-1})_5]$	13.96(13)
σ; n	1.31; 207



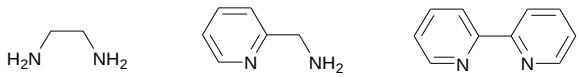
Scheme S1. Synthesis of Alaha (**3**). (a) CbzCl, NaOH (aq). (b) Ethylchloroformate, *N*-methylmorpholine, dichloromethane. (c) $H_{2(g)}$, Pd/C (10 %).



Scheme S2. Scheme of Picha 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).

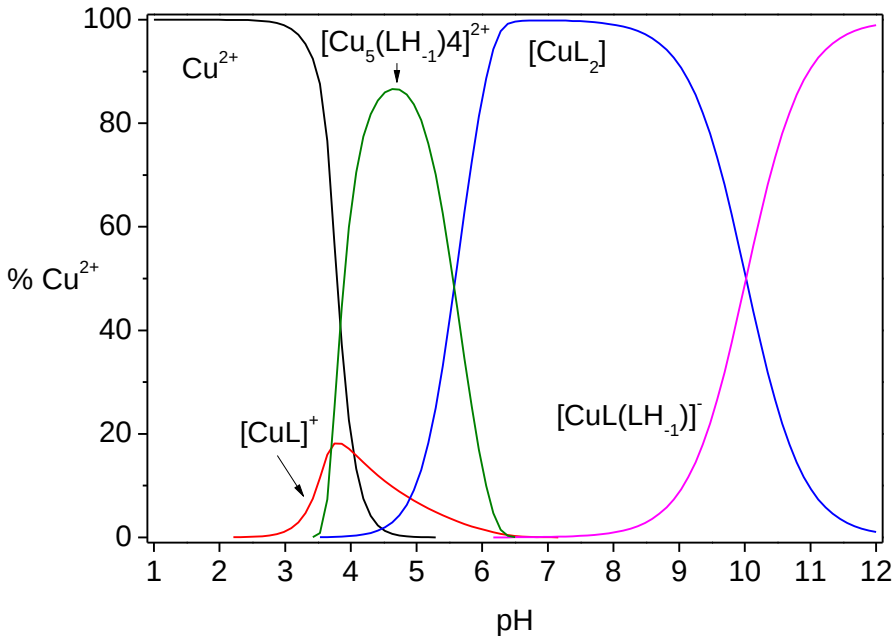


Figure S1. Representative speciation diagram of the system Cu(II) / Alaha (HL). Cu:L = 1:2.2, C_{Cu} = 2.8×10^{-3} mol L^{-1}, *I* = 0.1 mol L^{-1} (KCl), *T* = 298.2 K.

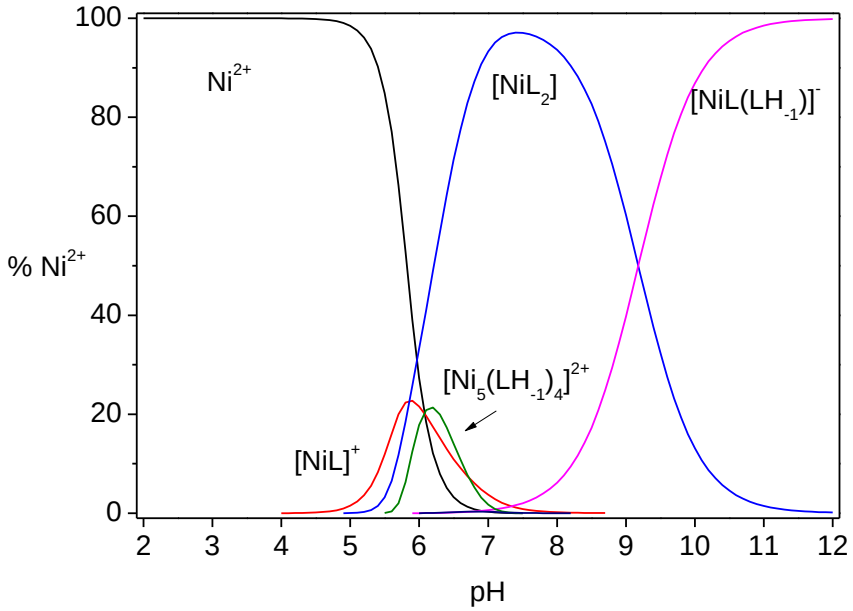


Figure S2. Representative speciation diagram of the system Ni(II) / Alaha (HL). Ni:L = 1:2.2, C_{Ni} = 2.8×10^{-3} mol L^{-1}, *I* = 0.1 mol L^{-1} (KCl), *T* = 298.2 K.

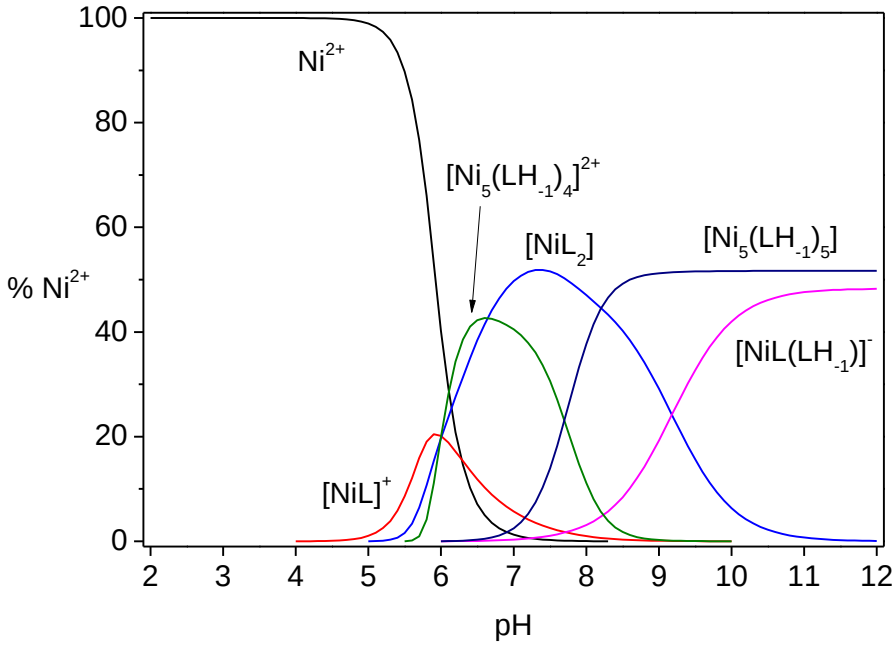


Figure S3. Representative speciation diagram of the system Ni(II) / Alaha (HL). Ni:L = 1:1.5, C_{Ni} = 2.8×10^{-3} mol L^{-1}, *I* = 0.1 mol L^{-1} (KCl), *T* = 298.2 K.

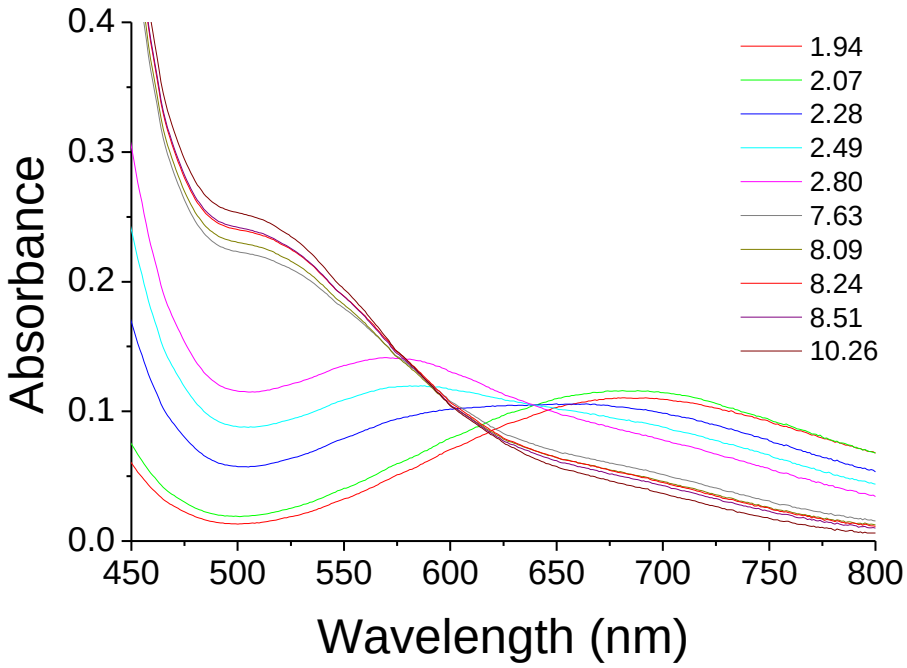


Figure S4. Experimental visible spectra for the system Cu(II) / Picha 1:2.17 (C_{Cu} = 2.31×10^{-3} mol L^{-1}, *I* = 0.1 M KCl) at different pH (see values in the inset).

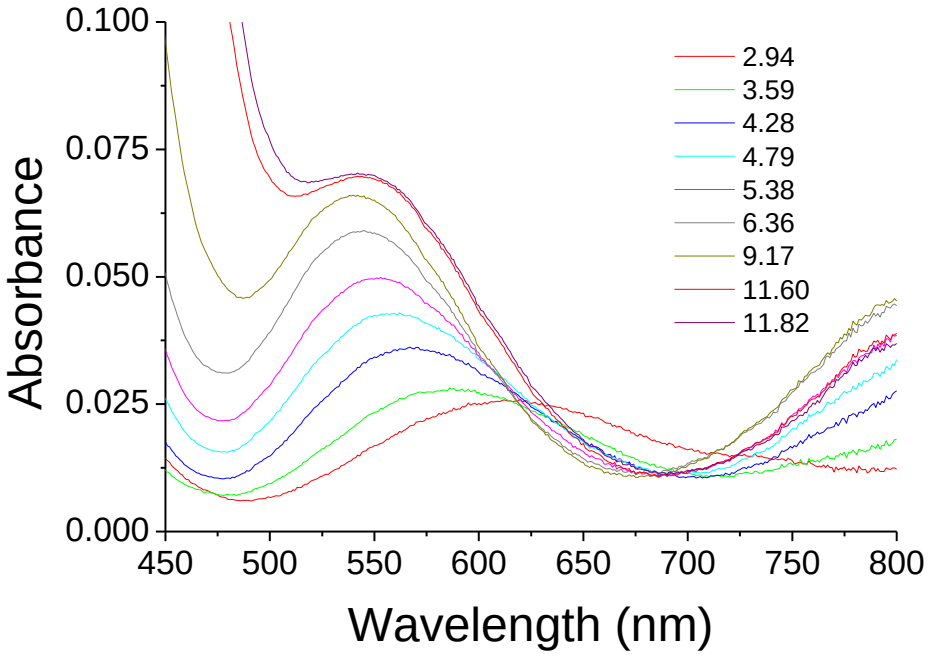


Figure S5. Experimental visible spectra for the system Ni(II) / Picha 1:2.73 (C_{Ni} = 3.67×10^{-3} mol L^{-1}, *I* = 0.1 M KCl) at different pH (see values in the inset).

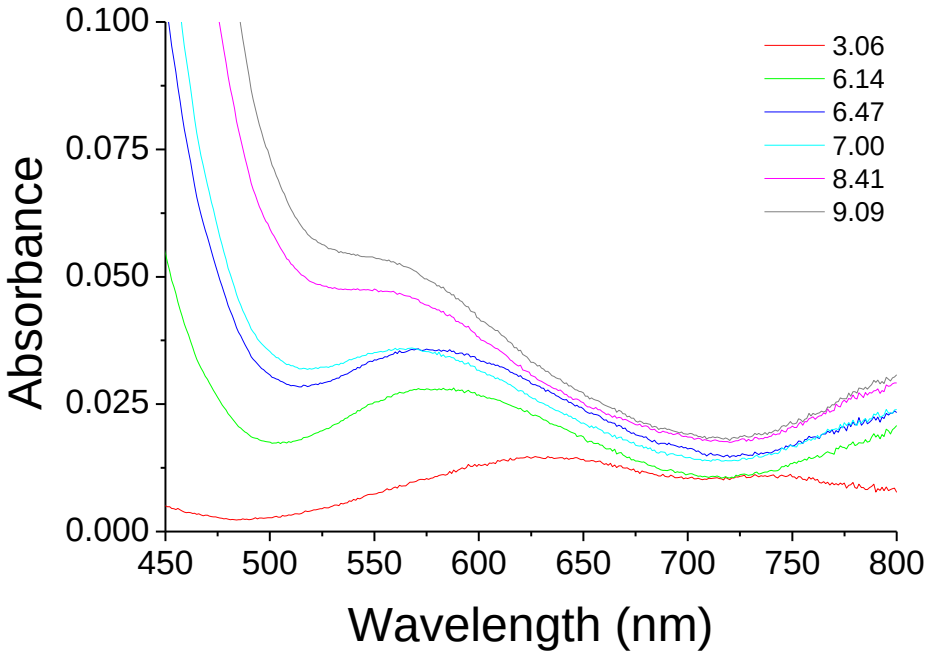


Figure S6. Experimental visible spectra for the system Ni(II) / Picha 1:1.45 (C_{Ni} = 3.67×10^{-3} mol L^{-1}, *I* = 0.1 M KCl) at different pH (see values in the inset).

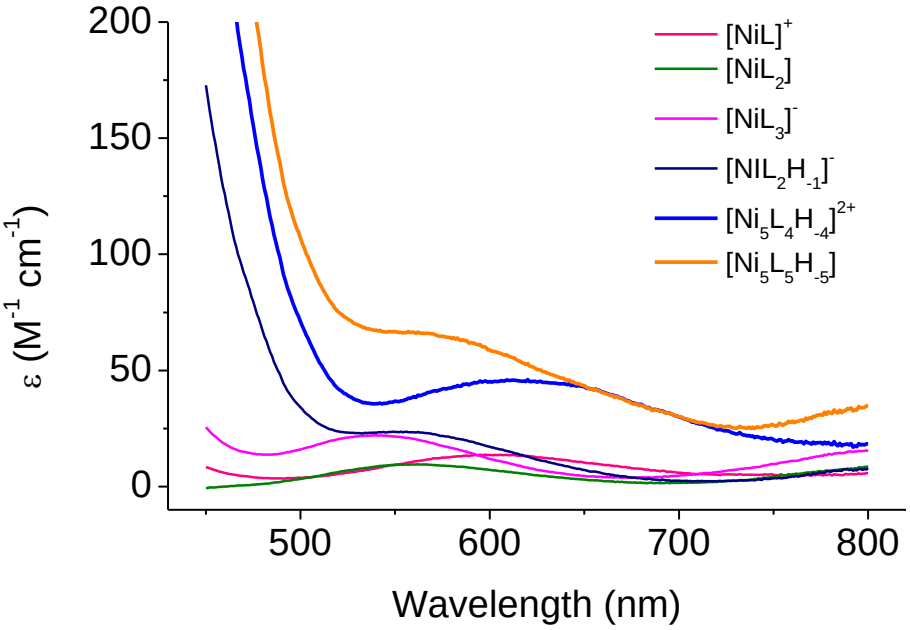


Figure S7. Calculated molar visible spectra for the complex species in the Ni(II) / Picha (HL) system, after the treatment with a speciation model which includes the 12-MC-4 complex. *I* = 0.1 mol L^{-1} (KCl), *T* = 298.2 K.

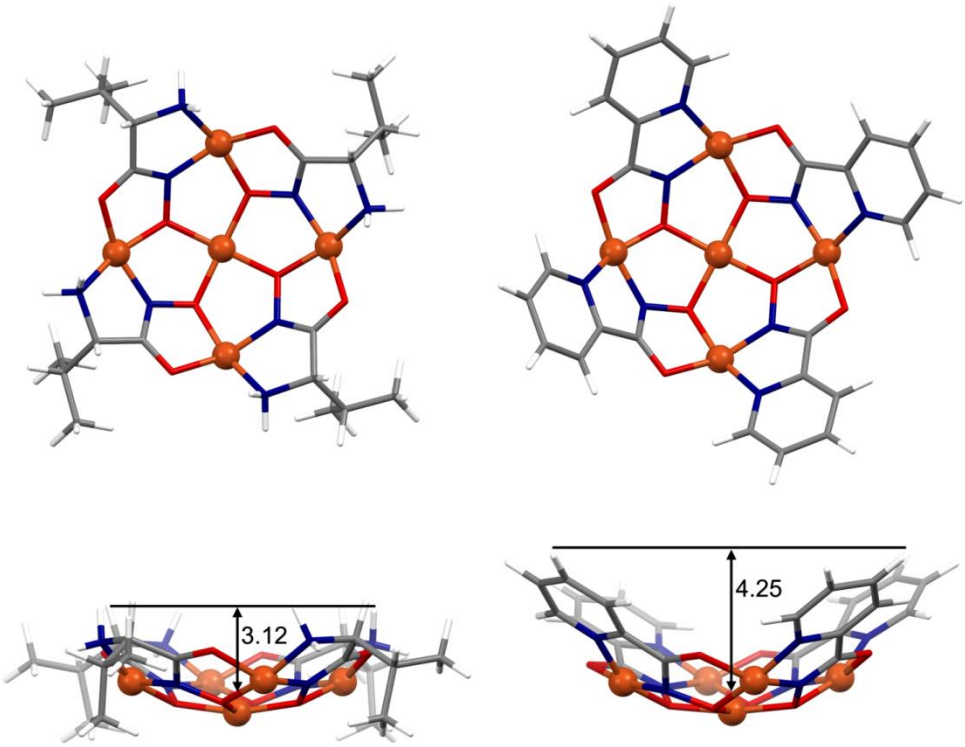


Figure S8. Comparison between of the optimized molecular structures (B3LYP/3-21G) of the 12-MC-4 $[Cu_5(LH_{-1})_4]^{2+}$ with HL = valinehydroxamic acid (Valha) (left) and HL = Picha (right).

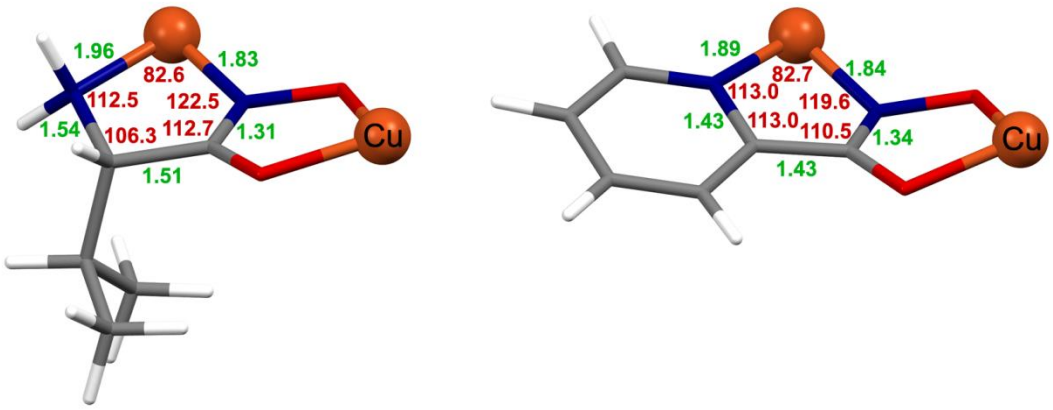


Figure S9. Comparison between the geometry of the valinehydroxamate (Valha) ligand (left) and of the ligand Picha (right) in the optimized structures of the respective 12-MC-4 $[Cu_5(LH_{-1})_4]^{2+}$. Bond distances (Å) in green and bond angles (°) in red.

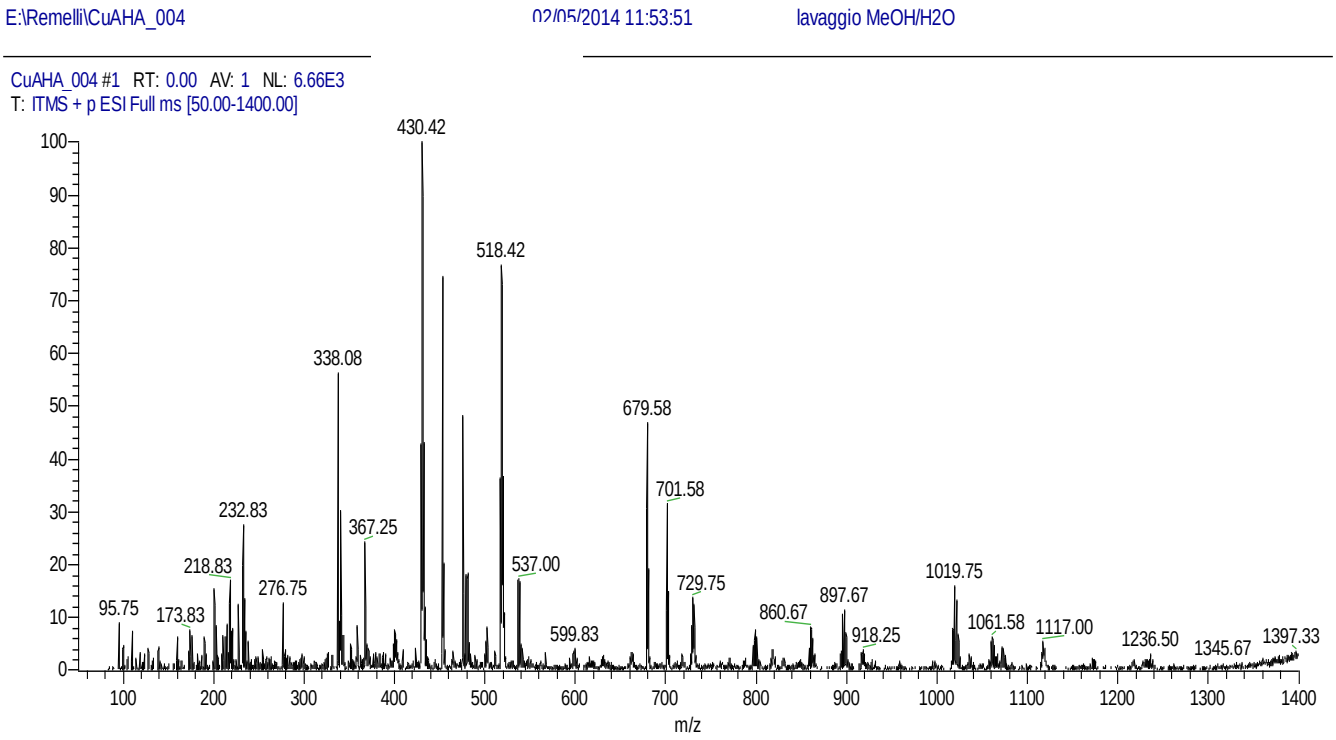


Figure S10. Positive ion ESI–MS spectrum for the complex of the system Cu(II)/PicHA 5:6 mM in aqueous solution, pH = 2.3.

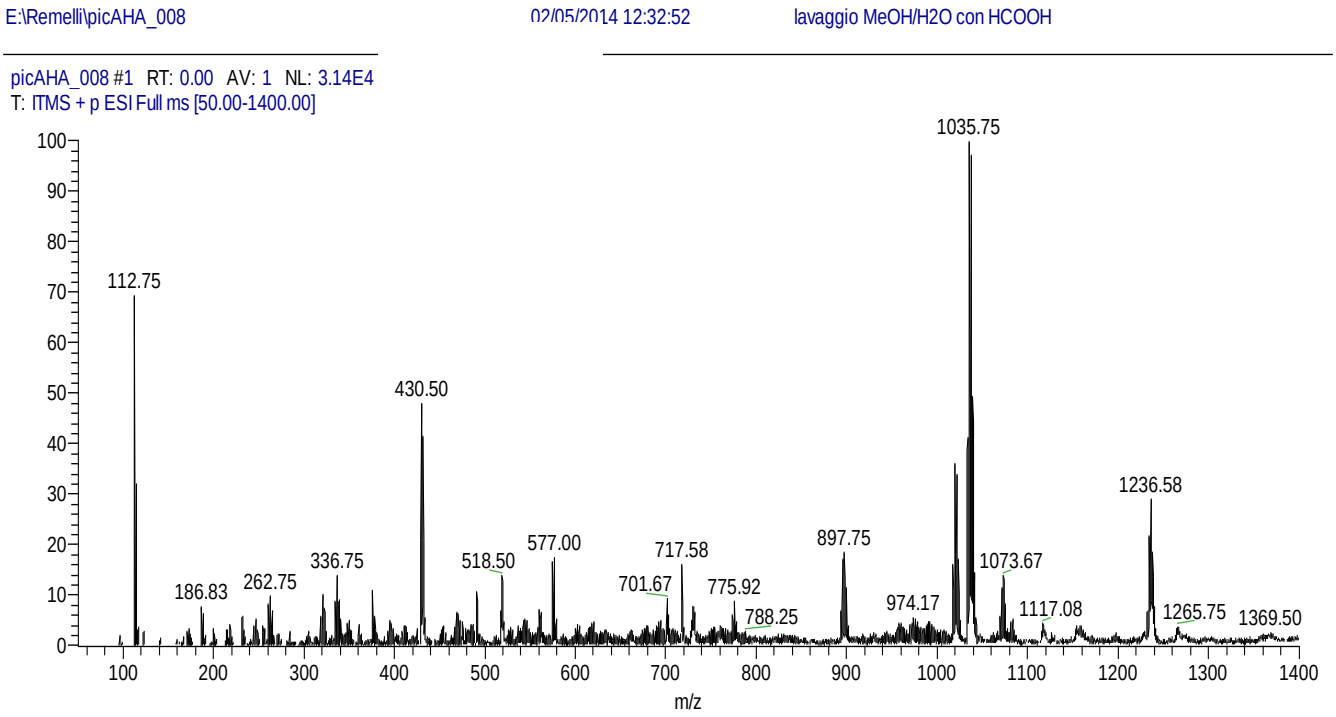


Figure S11. Positive ion ESI–MS spectrum for the complex of the system Cu(II)/PicHA 5:6 mM in aqueous solution, pH = 6.0.

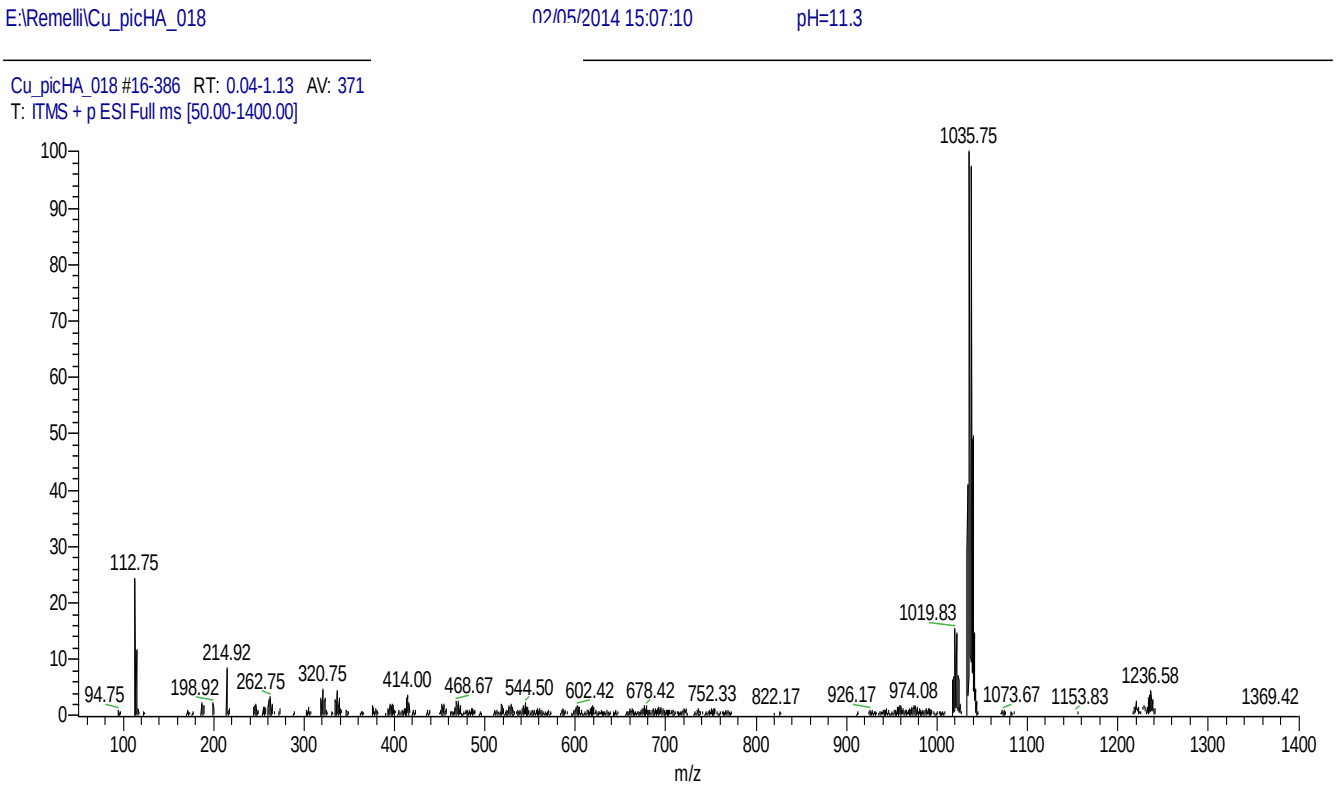


Figure S12. Positive ion ESI–MS spectrum for the complex of the system Cu(II)/PicHA 5:6 mM in aqueous solution, pH = 11.3.

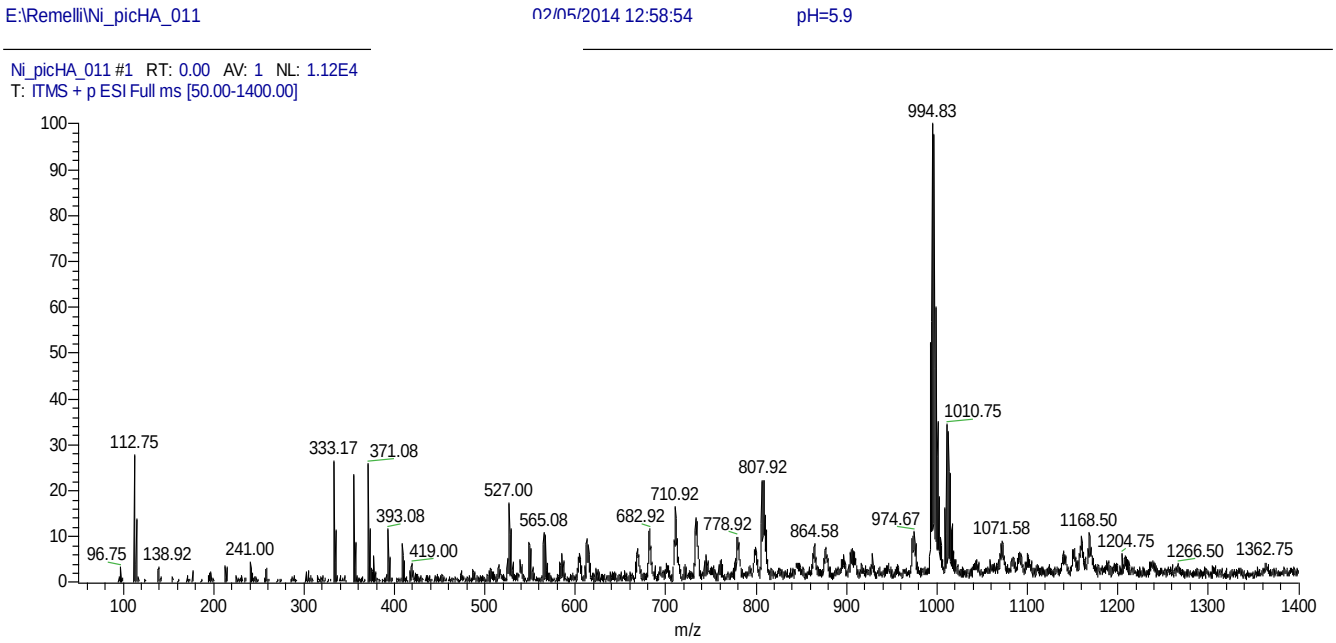


Figure S13. Positive ion ESI–MS spectrum for the complex of the system Ni(II)/PicHA 5:6 mM in aqueous solution, pH = 6.9.

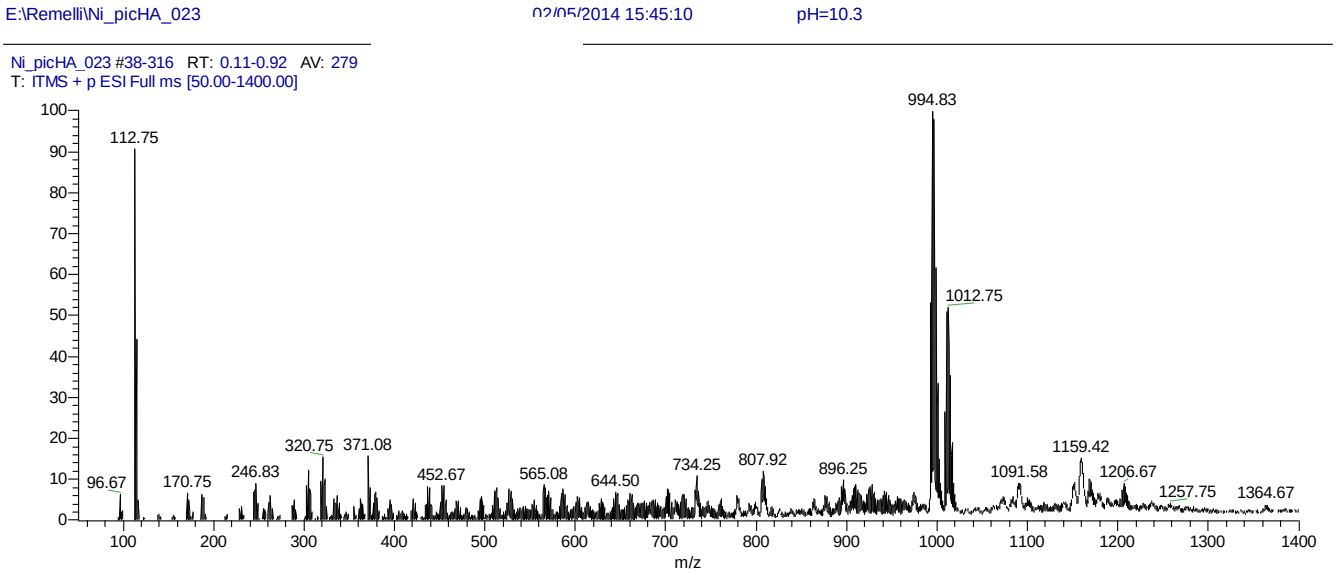


Figure S14. Positive ion ESI–MS spectrum for the complex of the system Ni(II)/PicHA 5:6 mM in aqueous solution, pH = 10.3.

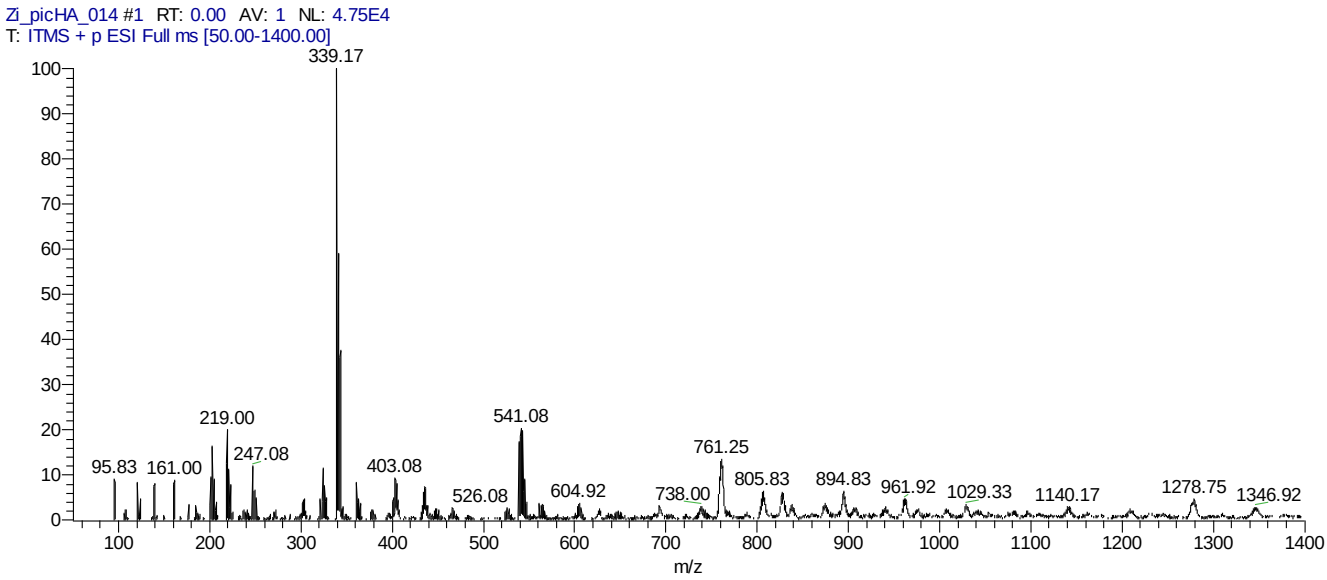


Figure S15. Positive-ion ESI–MS spectrum for the complex of the system Zn(II)/PicHA 5:6 mM in aqueous solution, pH = 6.0.

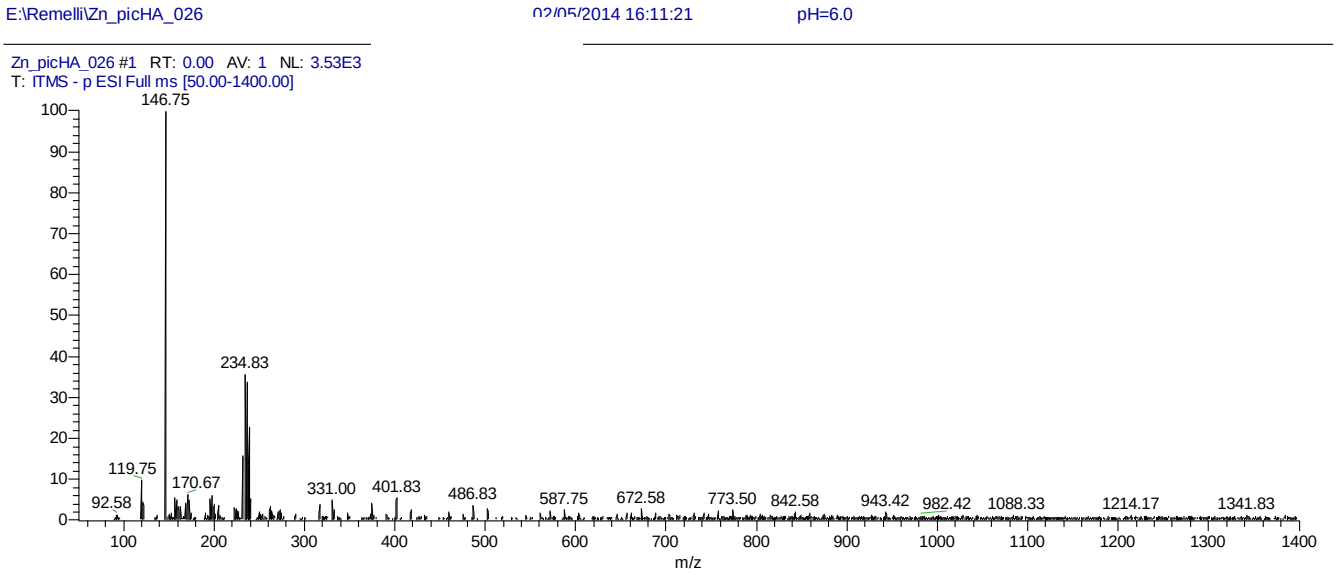


Figure S16. Negative-ion ESI–MS spectrum for the complex of the system Zn(II)/PicHA 5:6 mM in aqueous solution, pH = 6.0.

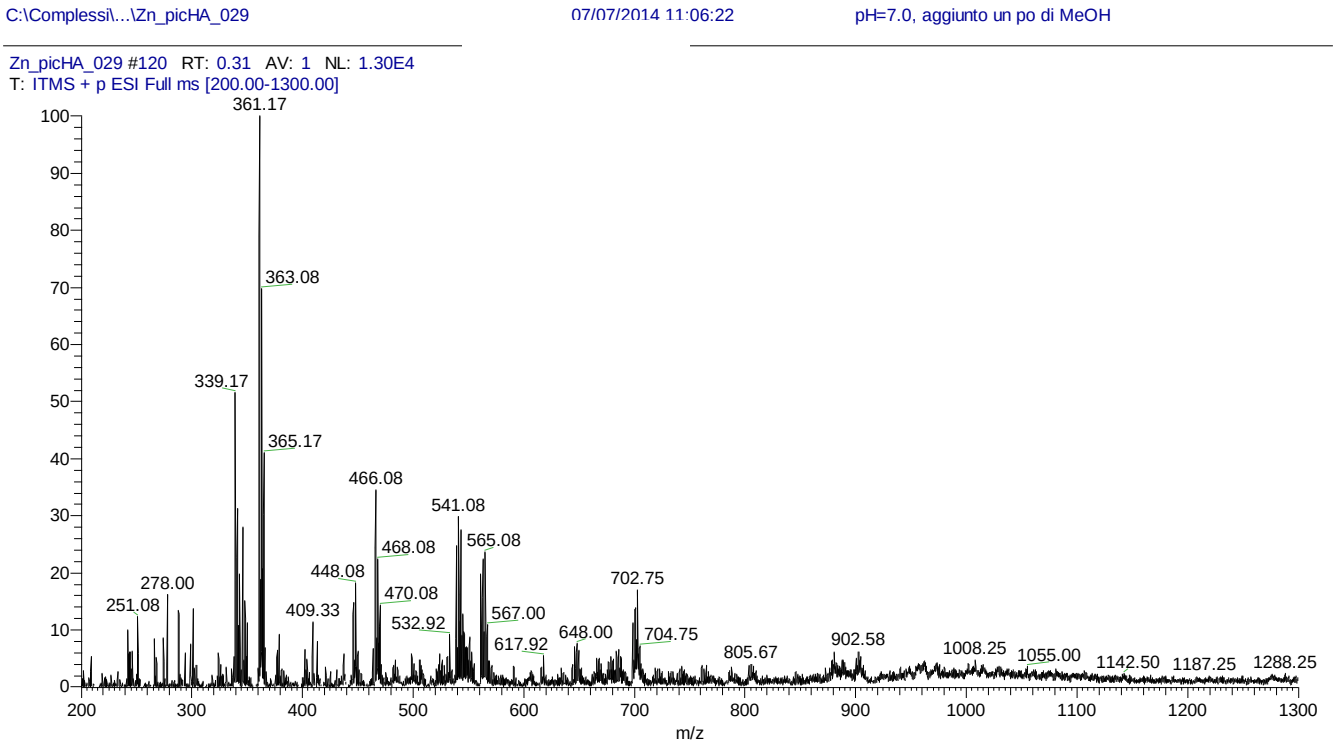


Figure S17. Positive-ion ESI–MS spectrum for the complex of the system Zn(II)/PicHA 5:8 mM in aqueous solution, pH = 7.0.

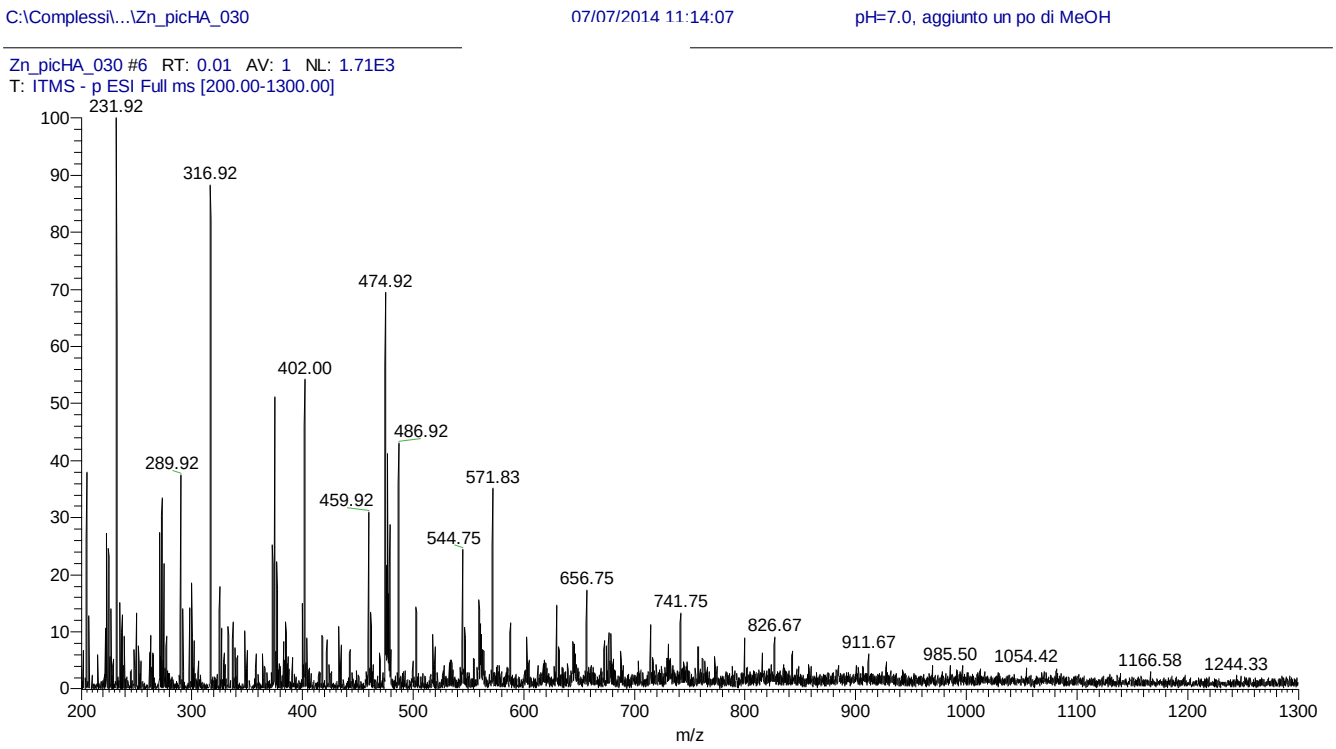


Figure S18. Negative-ion ESI–MS spectrum for the complex of the system Zn(II)/PicHA 5:8 mM in aqueous solution, pH = 7.0.

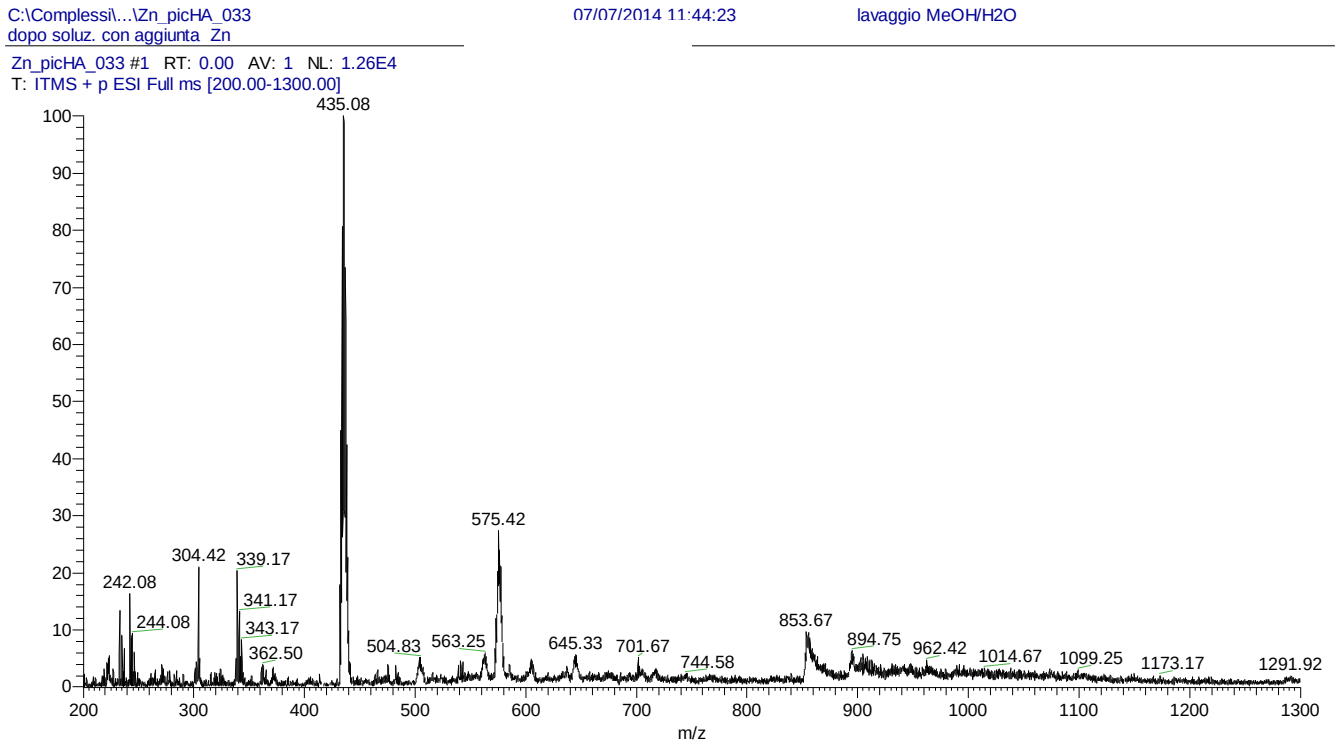


Figure S19. Positive-ion ESI–MS spectrum for the complex of the system Zn(II)/PicHA 8:8 mM in aqueous solution, pH = 6.3.

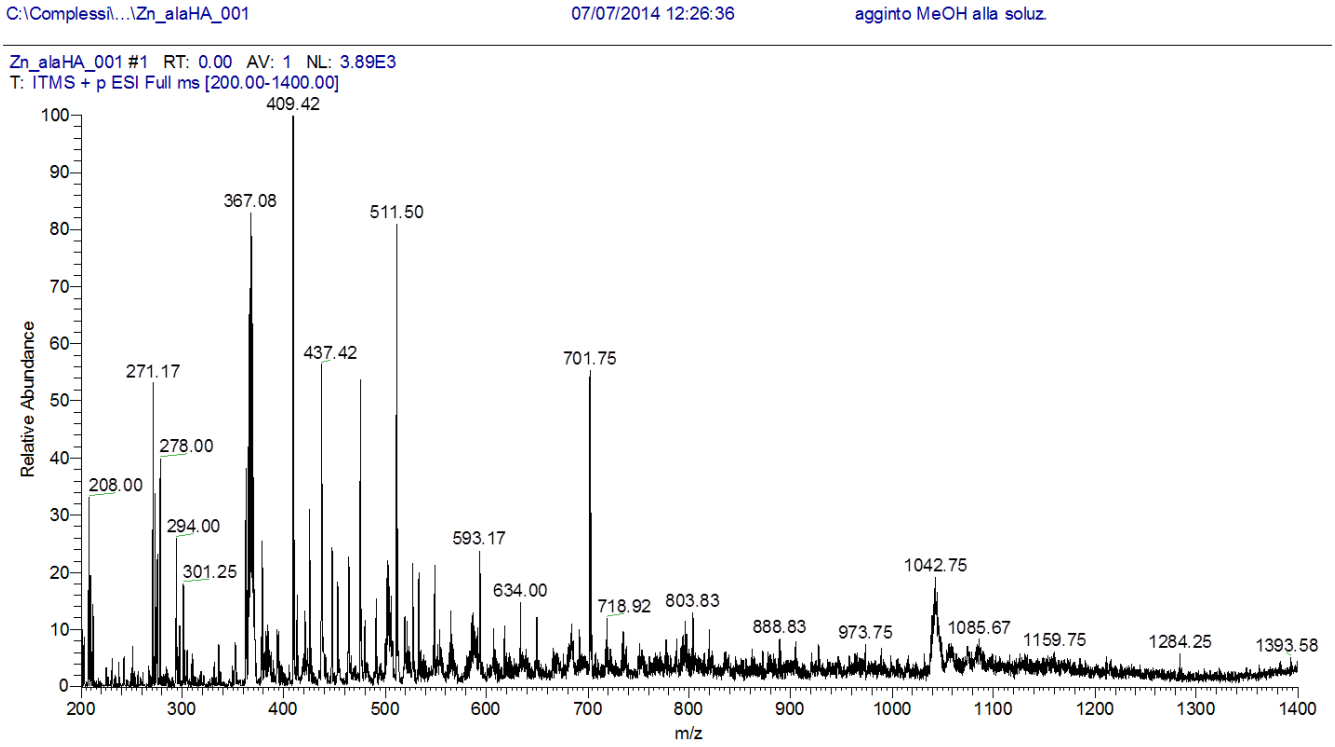


Figure S20. Positive-ion ESI–MS spectrum for the complex of the system Zn(II)/Alaha 5:6 mM in aqueous solution, pH = 7.2.