Stoichiometric diversity of Ni(II) metallacrowns with β-alaninehydroxamic acid in aqueous solution

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ELECTRONIC

SUPPLEMENTARY INFORMATION

Table S1. Thermodynamic parameters for the protonation of β-alaninehydroxamic acid, α-alaninehydroxamic acid and acetohydroxamic acid, in aqueous solution, at 298.2 ± 0.1 K e I = 0.1 mol·dm^{-3} (KCl). The standard deviation on the last figure is reported in parentheses.

Species	log β	log K	$-\Delta G^\bullet$ / kJ·mol^{-1}	$-\Delta H^\circ$ / kJ·mol^{-1}	$\Delta S^\bullet$ / J·mol^{-1}·K^{-1}
β-AlaHA[a]					
LH$_2^+$	18.12 (1)	8.39	103.4 (1)	62.8 (4)	136 (1)
LH	9.74 (1)	9.74	55.6 (1)	35.4 (3)	68 (1)
α-AlaHA[a]					
LH$_2^+$	16.48 (1)	7.33	94.1 (1)	62.8 (4)	105 (1)
LH	9.15 (1)	9.15	52.2 (1)	27.3 (4)	84 (1)
AHA[b]					
LH	9.35 (1)	9.35	53.3 (1)	22.4 (2)	104 (1)

[a] Data from M. Tegoni, M. Remelli, D. Bacco, L. Marchiò and F. Dallavalle, Dalton Trans., 2008, 2693.

[b] Data from M. Tegoni, L. Ferretti, F. Sansone, M. Remelli, V. Bertolasi and F. Dallavalle, Chemistry-.Eur. J., 2007, 13, 1300.

Table S2. ESI–MS ions for the complex species of the systems Ni(II)/β-AlaHA, obtained from spectra recorded at different pH. The *m/z* values refer to the most intense peak of each multiplet.

Species	m/z	pH
$[NiLH]Cl^+$	197	7.3
$[Ni(LH)L]^+$	265	7.3
$[NiL_2]Na^+$	287	8.5
$[NiL(LH_{-1})]Na_2^+$	309	11
$[Ni(LH_{-1})_2]Na_3^+$	331	11
$[Ni_5(LH_{-1})_4]^{2+}$	350	7.3, 8.5
$[Ni_5(LH_{-1})_4]Cl^+$	737	7.3, 7.5, 8.5, 11
$[Ni_4(LH_{-1})_4]Na^+$	665	8.5, 11
$[Ni_5(LH_{-1})_5]Na^+$	825	8.5, 11
$[Ni_6(LH_{-1})_6]Na^+$	987	8.5, 11
$[Ni_6(LH_{-1})_6]Na_2Cl^+$	1045	11

Table S3. Literature thermodynamic parameters for the formation of Ni(II) and Cu(II) complexes of α- and β-AlaHA, in aqueous solution, at 25°C e I = 0.1 M (KCl). The standard deviation on the last figure is reported in parentheses.

	log β	-$\Delta G°$ / kJ mol^{-1}	-$\Delta H°$ / kJ mol^{-1}	$\Delta S°$ / J K^{-1} mol^{-1}
α-AlaHA [a]				
[NiL]$^+$	6.88 (1)	39.2 (1)	13 (2)	92 (8)
[NiL$_2$]	14.05 (1)	80.1 (1)	24 (1)	187 (2)
[NiL(LH$_{-1}$)]$^-$	4.87 (3)	27.8 (2)	4 (1)	81 (4)
[Ni$_5$(LH$_{-1}$)$_4$]$^{2+}$	15.51 (5)	88.5 (3)	-21 (4)	367 (14)
[Ni$_5$(LH$_{-1}$)$_5$]	13.53 (8)	77.2 (5)	-27 (3)	350 (11)
α-AlaHA [b]				
[CuL]$^+$	10.76 (1)	61.4 (1)	33 (1)	95 (5)
[CuL$_2$]	19.84 (1)	113.2 (1)	66 (1)	158 (2)
[CuL(LH$_{-1}$)]$^-$	9.82 (1)	56.0 (1)	46 (1)	34 (3)
[Cu$_5$(LH$_{-1}$)$_4$]$^{2+}$	40.16 (1)	229.2 (1)	85 (3)	484 (9)
β-AlaHA [b]				
[CuLH]$^{2+}$	17.22 (2)	98.3 (1)	52 (1)	155 (2)
[Cu$_5$(LH$_{-1}$)$_4$]$^{2+}$	49.39 (7)	247.6 (4)	166 (3)	388 (9)

[a] Data from: D. Bacco, V. Bertolasi, F. Dallavalle, L. Galliera, N. Marchetti, L. Marchio, M. Remelli and M. Tegoni, *Dalton Trans.,* 2011, **40**, 2491.

[b] Data from: M. Careri, F. Dallavalle, M. Tegoni and I. Zagnoni, *J. Inorg. Biochem.*, 2003, **93**, 174.

Note 1

The stoichiometry of the $[NiLH]^{2+}$ complex is compatible with two alternative coordination modes of β-AlaHA to the Ni(II) ion: an (O,O^-) chelation with the amino group remaining protonated (Scheme 2a and 3a) or a monodentate coordination of the amine nitrogen to nickel leaving the hydroxamic group protonated and uncoordinated.

The formation constant value of the complex $[NiLH]^{2+}$ (14.04) is very close to the sum (14.27) of the two contributions due to the protonation of the amino group ($logK_{micro}$ = 8.85)[1] and the coordination of the hydroxamic acid group, as found for AHA ($log\beta_1$ = 5.42). These evidences support the first hypothesis ((O,O^-) chelation). The agreement is also reasonably good for enthalpic values: the formation $-\Delta H°$ value for $[NiLH]^{2+}$ (52.7 kJ·mol^{-1}) is well explained by the sum of the formation $-\Delta H°$ value for $[NiL]^+$ of AHA (8.8 kJ·mol^{-1}) and the $-\Delta H°$ value for the *micro* protonation of the amino group of β-AlaHA (41 kJ·mol^{-1}),[2] which actually sum up to 49.8 kJ·mol^{-1}. The second hypothesis (monodentate coordination) is ruled out by the analysis of the formation constants. Actually, the sum of the $log\beta_1$ value for $[NiL]^{2+}$ of n-propylamine ($log\beta_1$ = 2.81)[3] and of the protonation micro-constant of the hydroxamic group of β- AlaHA (8.47)[1] gives a predicted $log\beta$ for $[NiLH]^{2+}$ of 11.28 which is far from the experimental value.

References

1   E. Farkas, T. Kiss and B. Kurzak, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1255.

2   M. Tegoni, M. Remelli, D. Bacco, L. Marchiò and F. Dallavalle, *Dalton Trans.*, 2008, 2693.

3   L. D. Pettit and H. K. J. Powell, *The IUPAC Stability Constants Database*, Royal Society of Chemistry, London, 1992-2000.

Note 2

The deprotonation of the complex $[Ni(LH)_2]^{2+}$ to form $[NiL(LH)]^+$ is accompanied by a change of the coordination mode of β-AlaHA from (O,O^-) to (N,N^-). This coordination change does not occur when $[NiL_2]$ is formed. Actually, the pK value for the equilibrium $[Ni(LH)_2]^{2+} \leftrightarrows [NiL(LH)]^+ + H^+$ (7.37, Table 1) is lower than the calculated *micro*-constant for the amino group (8.85)[1] of about 1.5 units, thus suggesting that the release of the proton is accompanied and promoted by the coordination of the amino group to Ni(II). Moreover, this 1.5 log units difference is close to the difference between the log$β$ values of the 1:1 complexes of Ni(II)/AHA (5.42, Table 1) and of Ni(II)/ethylenediamine[2] (7.35) in comparable experimental conditions, again supporting a rearrangement of the ligand form the (O,O^-) to the (N,N^-) chelation mode. Similar considerations also apply to the $-ΔH°_{step}$ value for the same equilibrium: the expected value for a simple deprotonation of the amino group is -41 kJ·mol^{-1},[3] while here the deprotonation of $[Ni(LH)_2]^{2+}$ is less endothermic (-9.6 kJ·mol^{-1}, from data in Table 1). In our hypothesis, the deprotonation of the amino group is followed by the dissociation of a (O,O^-) chelate bond (formation $-ΔH°$= 8.8 kJ·mol^{-1} for the Ni(II)/AHA 1:1 species, Table 1) and rearrangement to form a $(N,N-)$ chelation ($-ΔH° = 37$ kJ·mol^{-1} for the Ni(II)/ethylenediamine 1:1 species).[2] Therefore the expected $-ΔH°_{step}$ value results $-41 - 8.8 + 37 = -15$ kJ·mol^{-1} which is in reasonable agreement with the experimental value of -9.6 kJ·mol^{-1}.

References

1   E. Farkas, T. Kiss and B. Kurzak, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1255.

2   L. D. Pettit and H. K. J. Powell, *The IUPAC Stability Constants Database*, Royal Society of Chemistry, London, 1992-2000.

3   M. Tegoni, M. Remelli, D. Bacco, L. Marchiò and F. Dallavalle, *Dalton Trans.*, 2008, 2693.

Note 3

$[NiL(LH_{-1})]^-$ and $[Ni(LH_{-1})_2]^{2-}$ cannot be hydroxo species as confirmed by the ESI-MS *m/z* data. The thermodynamic data are also in agreement with these observations. The pK_as of the two involved equilibria are 8.87 ($[NiL_2] \leftrightarrows [NiL(LH_{-1})]^- + H^+$) and 10.47 ($[NiL(LH_{-1})]^- \leftrightarrows [Ni(LH_{-1})_2]^{2-} + H^+$). As regards the first deprotonation, a very similar pK_a value (9.18) was observed for the same equilibrium for the Ni(II)/α-AlaHA system (Table S1, Supplementary Information). In that case, the $[NiL_2]$ complex has a bis-*(N,N-)* chelation geometry and the dissociation occurs on one hydroxamic OH with formation of an intramolecular hydrogen-bond, as confirmed by crystallographic data.[1] Here we put forward a similar hypothesis: the dissociation occurs on one hydroxamic group and is accompanied by a change of geometry of the complex from *(O,O⁻,N,N⁻)* to cis-*(N,N⁻,N,N⁻)* which allows for the formation of a intramolecular O⋯H⋯O hydrogen bond. This accounts for both the low pK_a of $[NiL_2]$ (8.87) and the higher pK_a for the last deprotonation step. In fact, under this hypothesis, the release of the last proton will lead to the cleavage of the hydrogen bond. Possibly, we might also expect a simultaneous rearrangement of the ligands in trans, due to a lower steric hindrance.

References

1   D. Bacco, V. Bertolasi, F. Dallavalle, L. Galliera, N. Marchetti, L. Marchio, M. Remelli and M. Tegoni, *Dalton Trans.*, 2011, **40**, 2491.
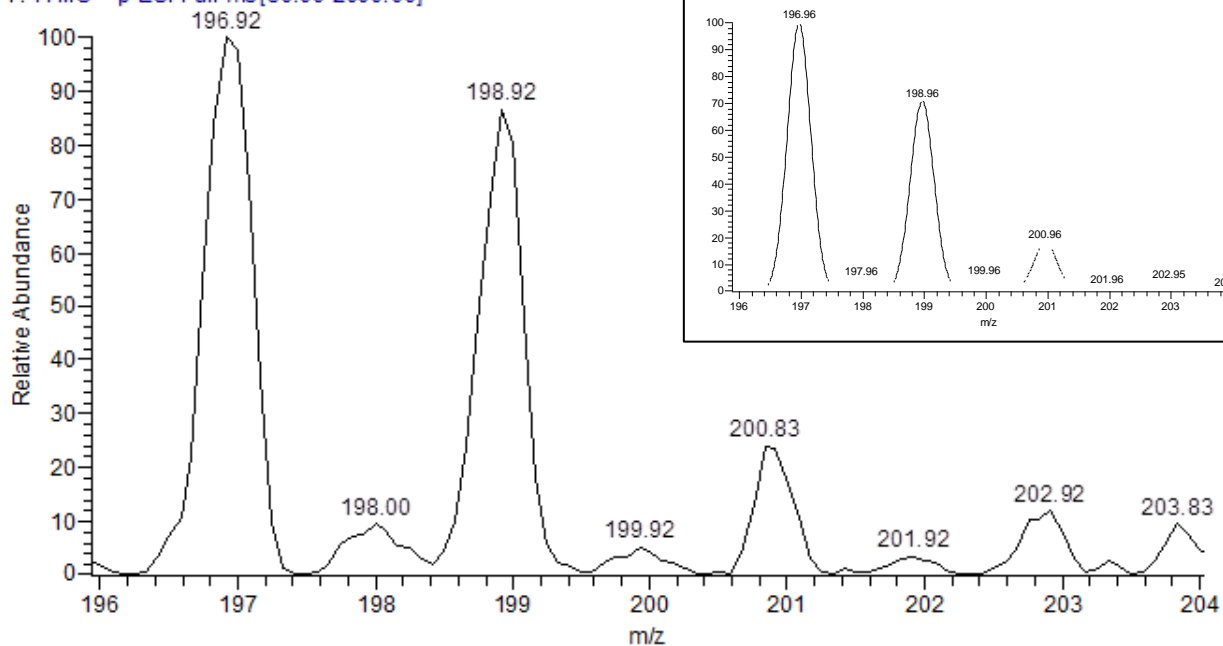
Fig. S1. Experimental and simulated (inset) ESI–MS spectrum for the complex $[NiLH]Cl^{+}$ (m/z = 197) in the Ni(II) / β-Alaha system, in aqueous solution, at pH 7.3.

Ni_bala_3_001   010 16.49.08   soluz. 3

Ni_bala_3_001 #1 RT: 0.00 AV: 1 NL: 6.40E
T: ITMS + p ESI Full ms [50.00-2000.00]
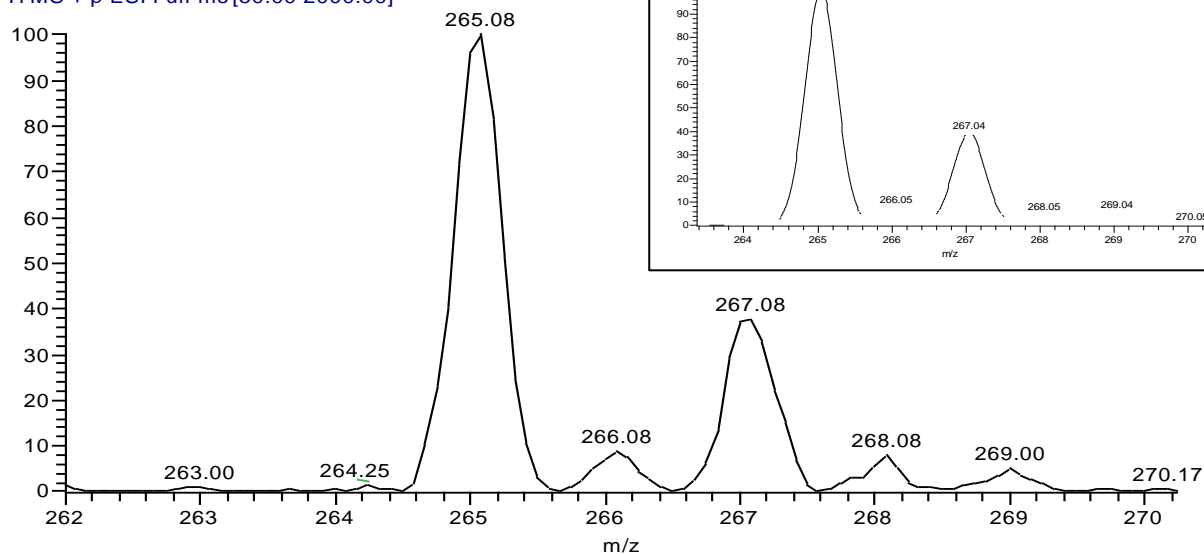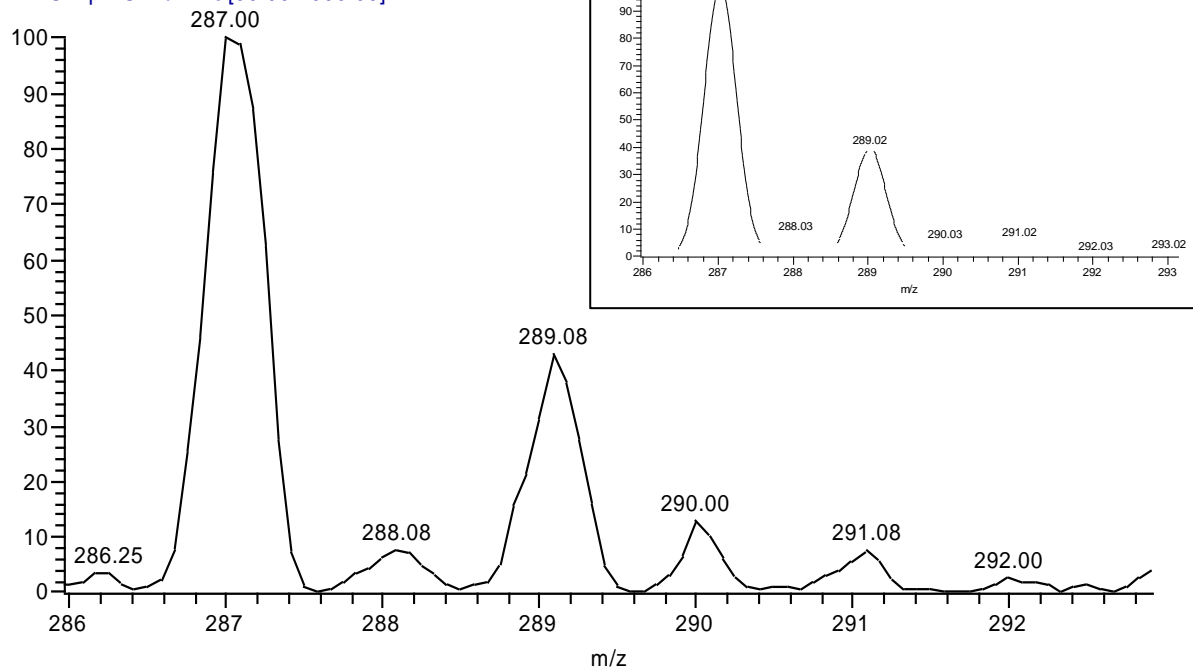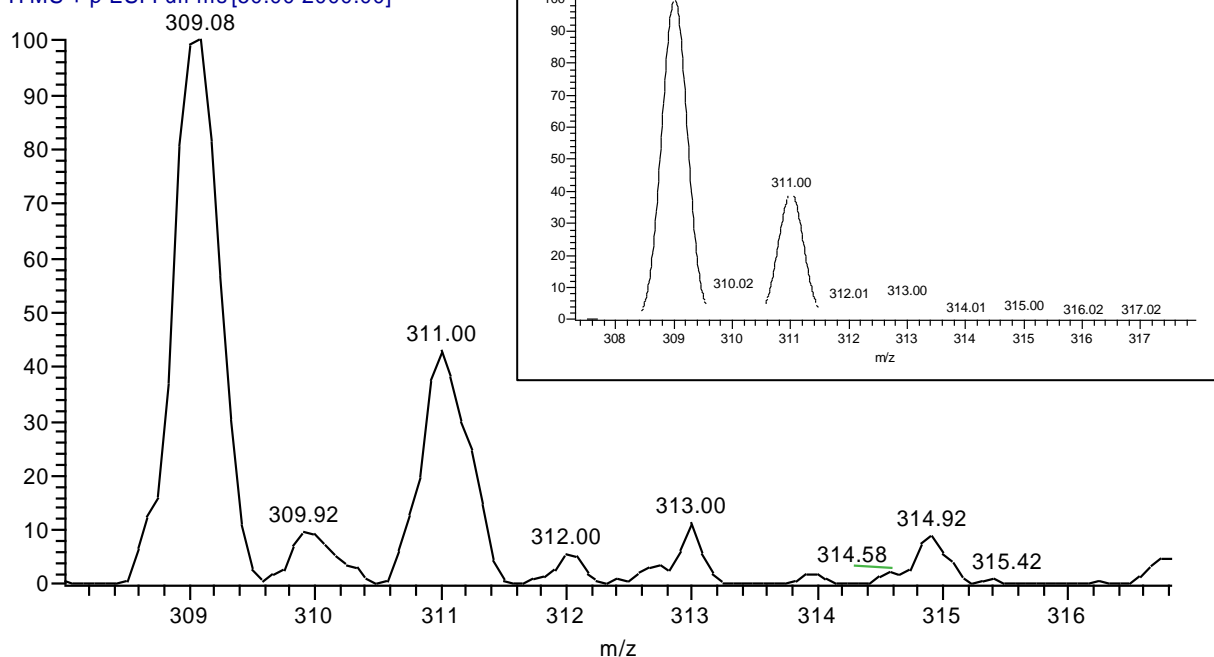

Fig. S2. Experimental and simulated (inset) ESI–MS spectrum for the complex $[Ni(LH)L]^+$ (m/z = 265) in the Ni(II) / β-Alaha system, in aqueous solution, at pH 7.3.

Ni_bala_4_002   10 15.46.03   soluz. 4

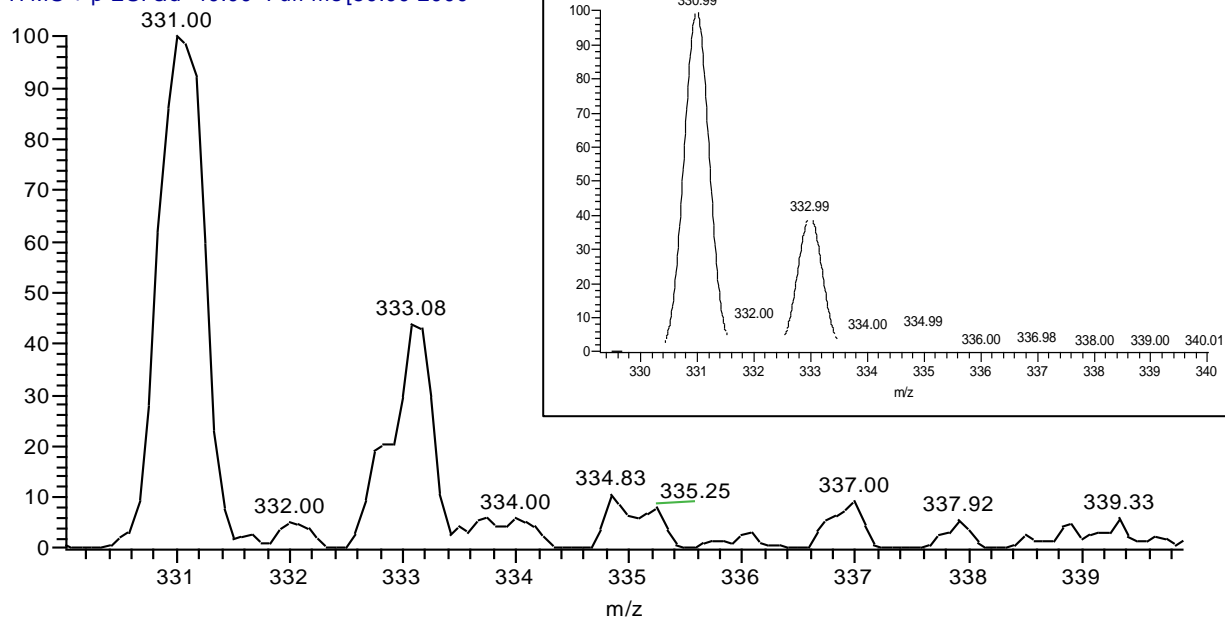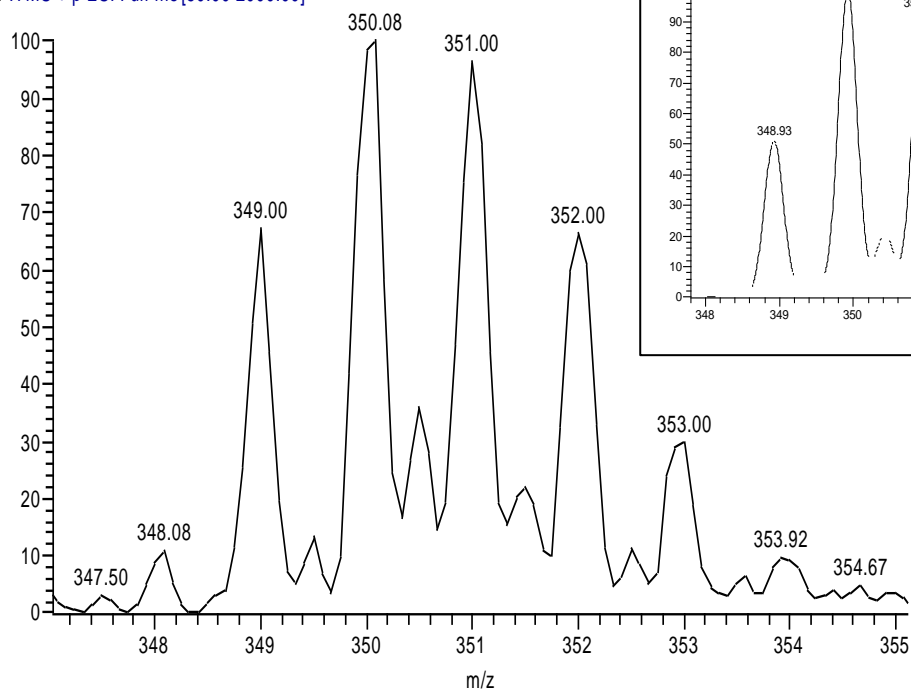Ni_bala_4_002 #1 RT: 0.00 AV: 1 NL: 4.58E
T: ITMS + p ESI Full ms [50.00-2000.00]

Fig. S3. Experimental and simulated (inset) ESI–MS spectrum for the complex $[NiL_2]Na^+$ (m/z = 287) in the Ni(II) / β-Alaha system, in aqueous solution, at pH 8.5.

Ni_bala_2_002   10 16.43.52   soluz. 2

Ni_bala_2_002 #1 RT: 0.00 AV: 1 NL: 2.23E
T: ITMS + p ESI Full ms [50.00-2000.00]

Fig. S4. Experimental and simulated (inset) ESI–MS spectrum for the complex $[NiL(LH_{-1})]Na_2^+$ (m/z = 309) in the Ni(II) / β-Alaha system, in aqueous solution, at pH 11.

Ni_bala_2_001   10 15.32.26   soluz. 2

Ni_bala_2_001 #1 RT: 0.00 AV: 1 NL: 1.50E
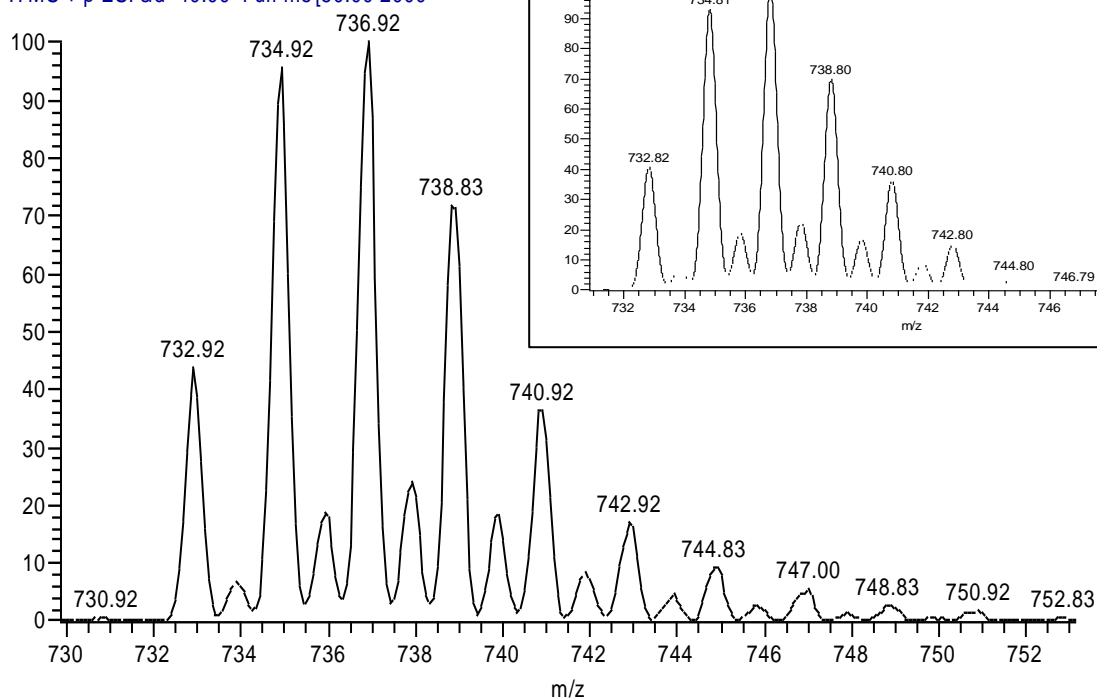T: ITMS + p ESI sid=40.00 Full ms [50.00-2000

Fig. S5. Experimental and simulated (inset) ESI–MS spectrum for the complex $[Ni(LH_{-1})_2]Na_3^+$ (m/z = 331) in the Ni(II) / β-Alaha system, in aqueous solution, at pH 11.

Ni_bala_3_001   10 16.49.08   soluz. 3

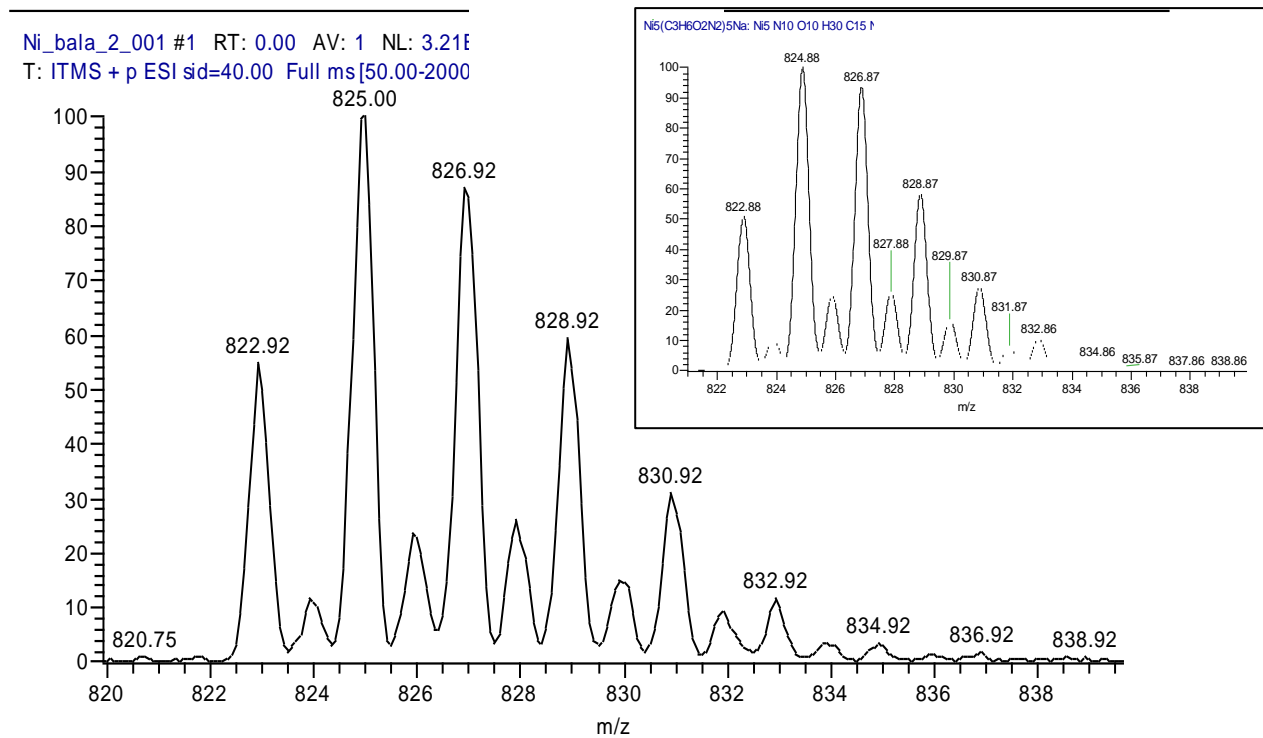Ni_bala_3_001 #1 RT: 0.00 AV: 1 NL: 3.34E
T: ITMS + p ESI Full ms [50.00-2000.00]

Fig. S6. Experimental and simulated (inset) ESI–MS spectrum for the complex $[Ni_5(LH_{-1})_4]^{2+}$ (m/z = 350) in the Ni(II) / β-Alaha system, in aqueous solution, at pH 7.3.

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Fig. S7. Experimental and simulated (inset) ESI–MS spectrum for the complex $[Ni_5(LH_{-1})_4]Cl^+$ (m/z = 737) in the Ni(II) / β-Alaha system, in aqueous solution, at pH 7.5.

Fig. S8. Experimental and simulated (inset) ESI–MS spectrum for the complex $[Ni_5(LH_{-1})_5]Na^+$ (m/z = 825) in the Ni(II) / β-Alaha system, in aqueous solution, at pH 11.

Ni_bala_2_001   '10 15.32.26   soluz. 2

Ni_bala_2_001 #1 RT: 0.00 AV: 1 NL: 2.92E
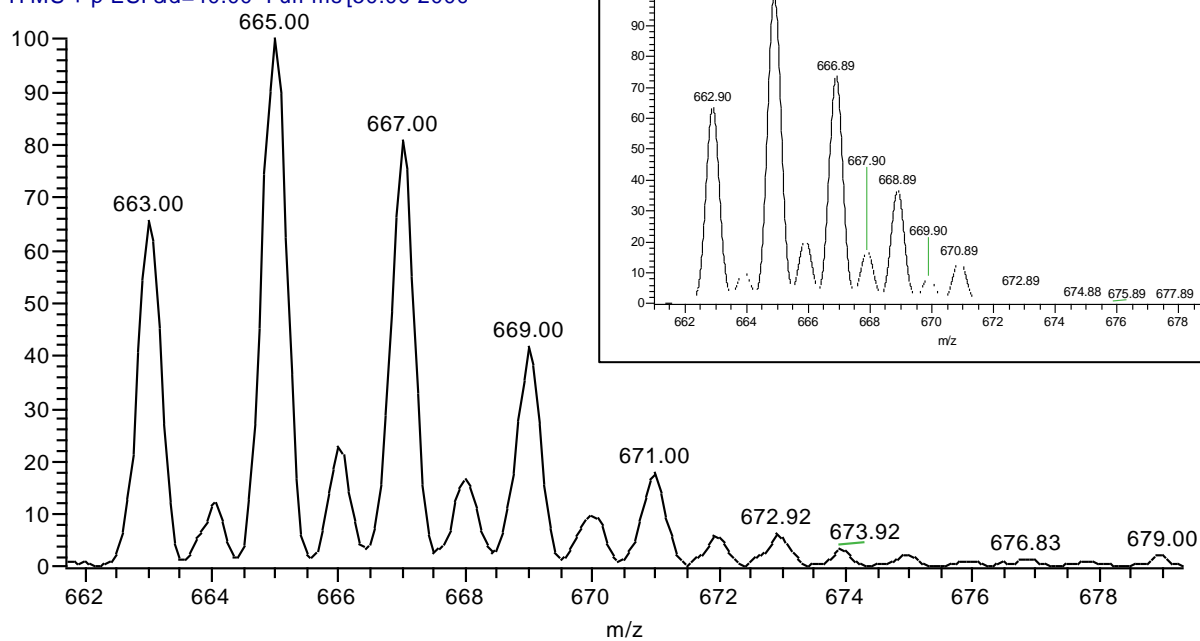T: ITMS + p ESI sid=40.00 Full ms [50.00-2000

Fig. S9. Experimental and simulated (inset) ESI–MS spectrum for the complex $[Ni_4(LH_{-1})_4]Na^+$ (m/z = 665) in the Ni(II) / β-Alaha system, in aqueous solution, at pH 11.

Ni_bala_2_001   ›10 15.32.26   soluz. 2

Ni_bala_2_001 #1 RT: 0.00 AV: 1 NL: 8.18E
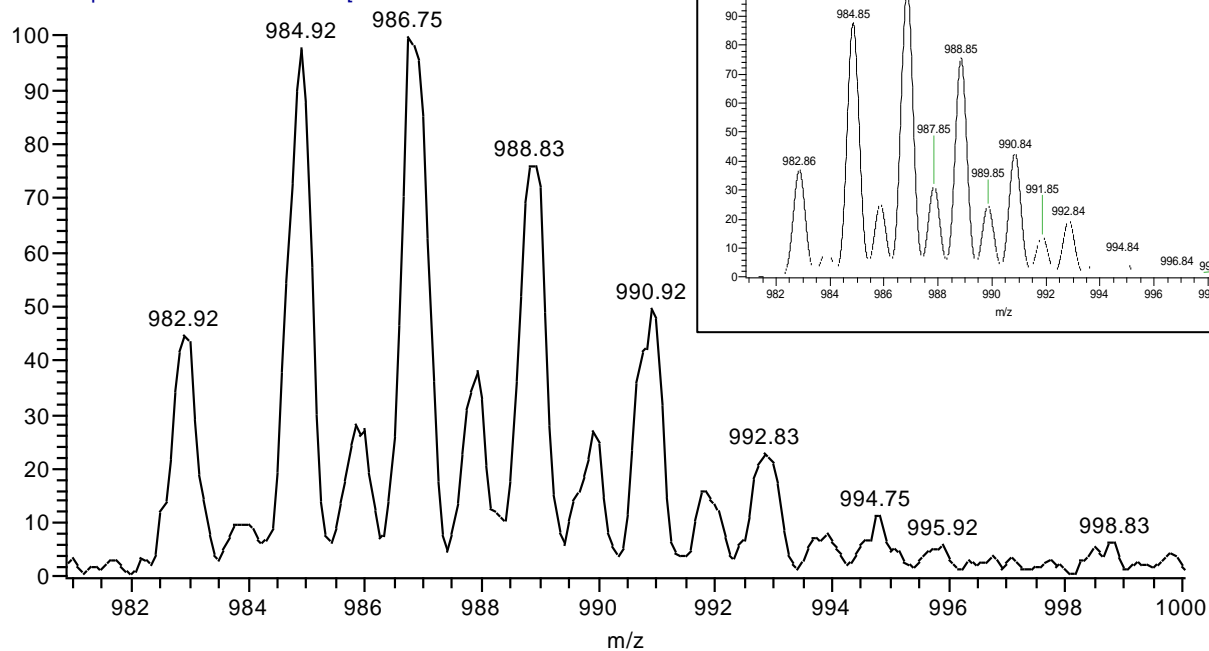T: ITMS + p ESI sid=40.00 Full ms [50.00-2000

Fig. S10. Experimental and simulated (inset) ESI–MS spectrum for the complex $[Ni_6(LH_{-1})_6]Na^+$ (m/z = 987) in the Ni(II) / β-Alaha system, in aqueous solution, at pH 11.
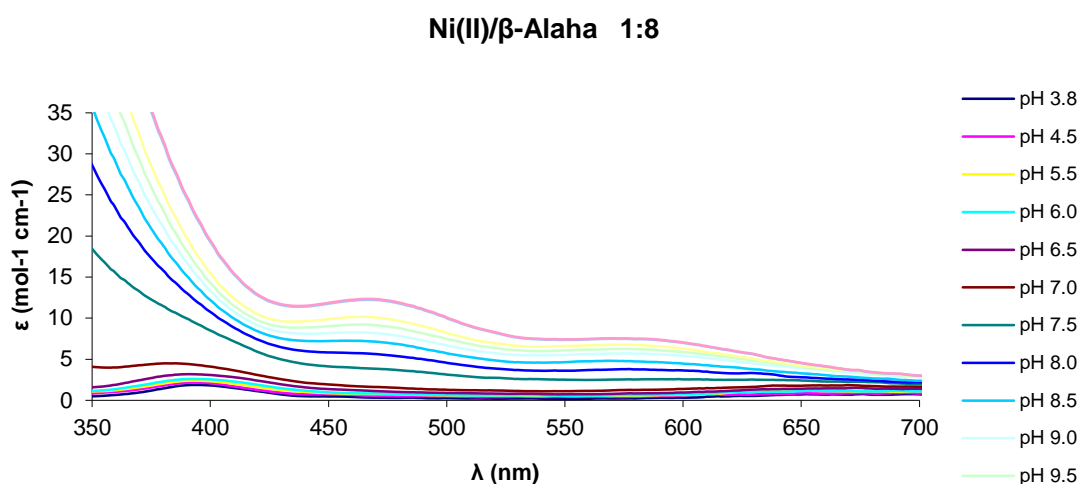
Ni(II)/β-Alaha   1:8

Fig. S11. Experimental UV-Vis spectra at variable pH for the system Ni(II) / β-Alaha, in aqueous solution. $C°_M = 0.01$ M, $C°_L = 0.08$ M.
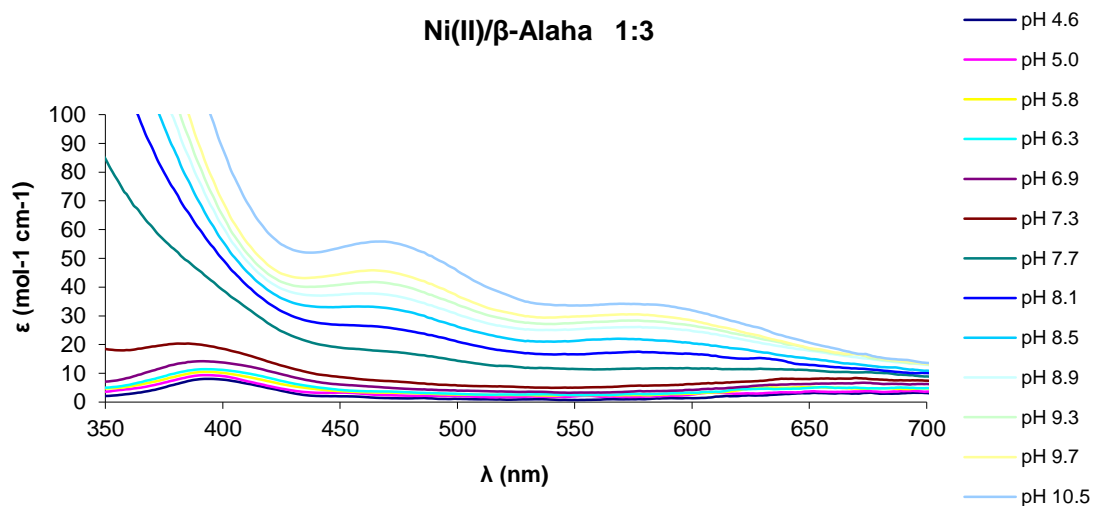
Ni(II)/β-Alaha   1:3

Fig. S12. Experimental UV-Vis spectra at variable pH for the system Ni(II) / β-Alaha, in aqueous solution. $C°_M = 0.0024$ M, $C°_L = 0.0076$ M.
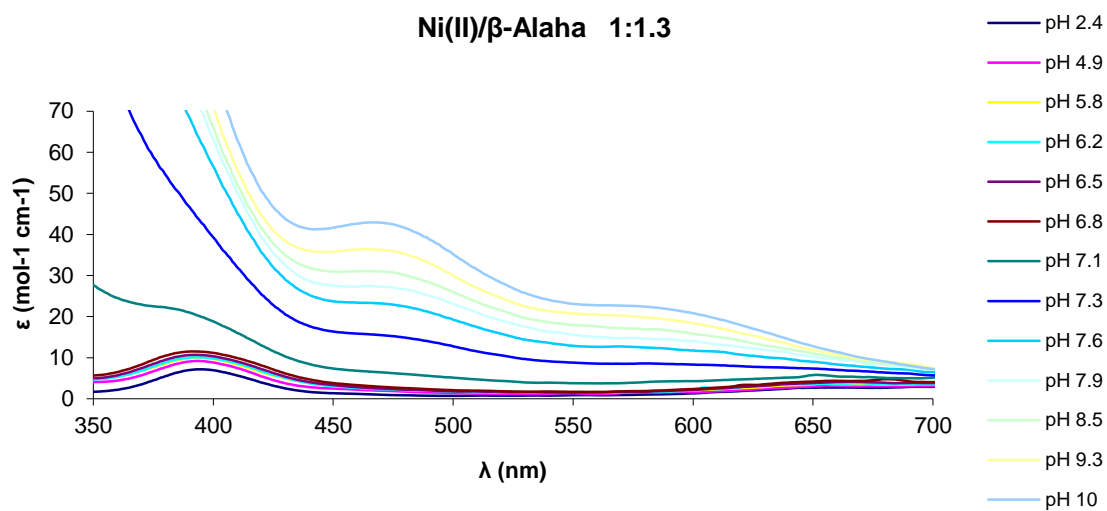
Ni(II)/β-Alaha   1:1.3

Fig. S13. Experimental UV-Vis spectra at variable pH for the system Ni(II) / β-Alaha, in aqueous solution. $C°_M = 0.008$ M, $C°_L = 0.010$ M.