METALLACROWNS OF Ni(II) WITH α-AMINOHYDROXAMIC ACIDS IN AQUEOUS SOLUTION: BEYOND A 12-MC-4, AN UNEXPECTED (VACANT?) 15-MC-5

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SUPPLEMENTARY INFORMATION

Scheme S1 Structures of the aminohydroxamic acids (S)-α-Alaha (left) and (S)-Valha (right).

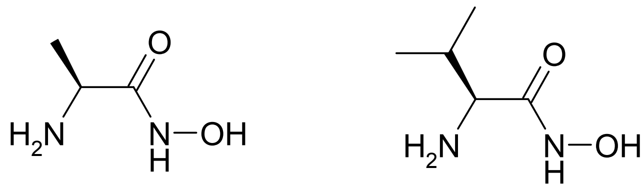


Table S1 Overall thermodynamic complex-formation parameters in the system Cu^{2+}/α-Alaha. Data from M. Tegoni, F. Dallavalle, B. Belosi, M. Remelli, Dalton Trans. **2004**, 1329-1333.

SPECIES	log β	-ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})
$[CuL]^+$	10.76	33	95
$[CuL_2]$	19.84	66	158
$[CuL_2H_{-1}]^-$	9.82	46	34
$[Cu_5L_4H_{-4}]^{2+}$	40.16	85	484

Table S2 Overall thermodynamic parameters for protonation of α-Alaha, (*R,S*)-Valha and acetohydroxamic acid (Acha) in aqueous solution. T = 298.2 K, I = 0.1 mol dm^{-3}. Background electrolytes: KCl, NaCl or $(C_2H_5)_4NCl$. Standard deviation on last figure is given in parentheses. Literature data from Tegoni, M., L. Ferretti, et al. (2007), Chem-Eur. J., 13(4): 1300-1308 and Tegoni, M., M. Remelli, et al. (2008), Dalton Trans., (20): 2693-2701..

Species	log β	-$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}	log $\beta^{\#}$	log $\beta^{\#}$
α-Alaha	KCl			NaCl	$(C_2H_5)_4NCl$
LH	9.15 (1)	27.3 (4)	84 (1)	9.07 (2)	9.27 (1)
LH_2^+	16.48 (1)	62.8 (4)	105 (1)	16.36 (3)	16.62 (1)
(*R,S*)-Valha	KCl				
LH	9.22 (1)	24.3 (9)	95 (3)	-	-
LH_2^+	16.43 (1)	57 (1)	123 (4)	-	-
Acha	KCl				
LH	9.35 (1)	22.4 (2)	104.0 (6)	-	-

This work

Figure S1 Time resolved Vis Spectra. Ni^{2+} / α-Alaha 1 : 1.2; $C°_{Ni}$ = 6 mmol dm^{-3}, pH = 8.5.

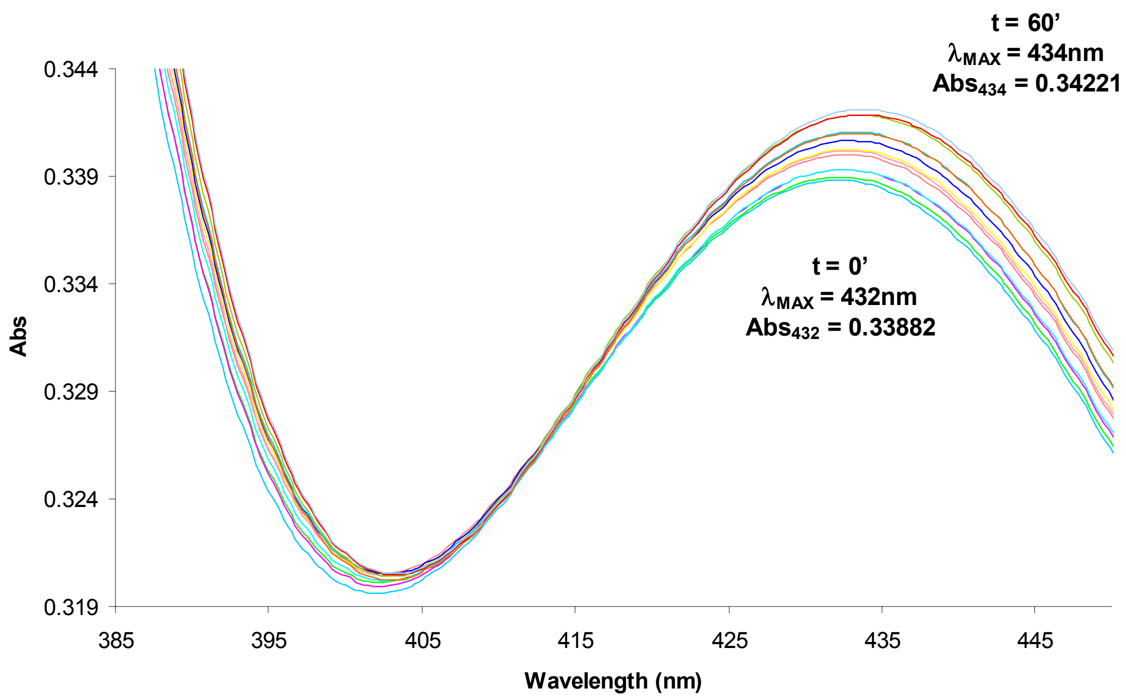
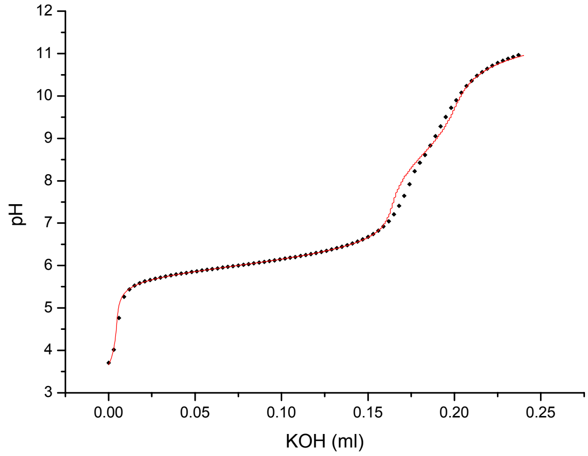
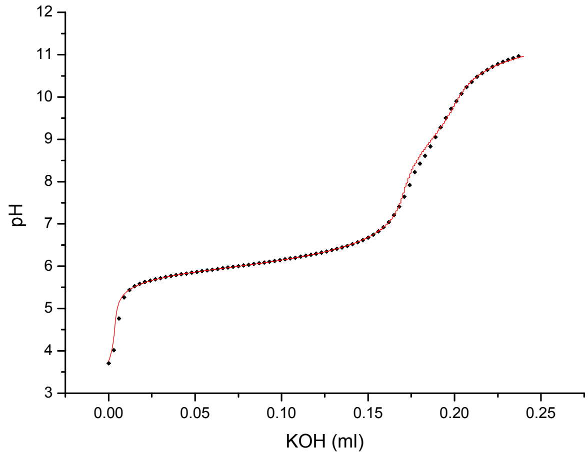


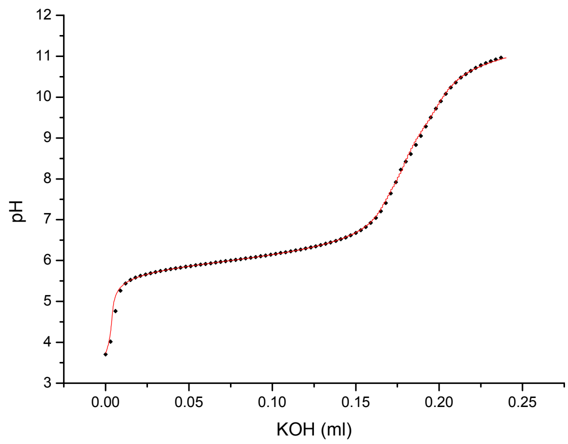
Figure S2. Example of curve fitting using different speciation models. System: Ni^{2+} / α-Alaha 1 : 1.5; $C°_{Ni}$ = 4.4 mmol dm^{-3}; T = 298.2 K, I = 0.1 mol dm^{-3} (KCl). Black symbols: experimental data; red line: fitting curve.



Species	log β
$[NiL]^+$	6.74 (2)
$[NiL_2]$	14.07 (1)
$[NiL_2H_{-1}]^-$	5.49 (1)
$[Ni_5L_4H_{-4}]^{2+}$	-
$[Ni_5L_5H_{-5}]$	-
σ	3.14
χ^2	75.1
n	370



Species	log β
$[NiL]^+$	6.92 (7)
$[NiL_2]$	13.95 (1)
$[NiL_2H_{-1}]^-$	5.00 (2)
$[Ni_5L_4H_{-4}]^{2+}$	15.65 (3)
$[Ni_5L_5H_{-5}]$	-
σ	2.00
χ^2	16.0
n	370



Species	log β
$[NiL]^+$	6.88 (1)
$[NiL_2]$	14.05 (1)
$[NiL_2H_{-1}]^-$	4.88 (3)
$[Ni_5L_4H_{-4}]^{2+}$	15.51 (5)
$[Ni_5L_5H_{-5}]$	13.53 (8)
σ	1.89
χ^2	8.3
n	370

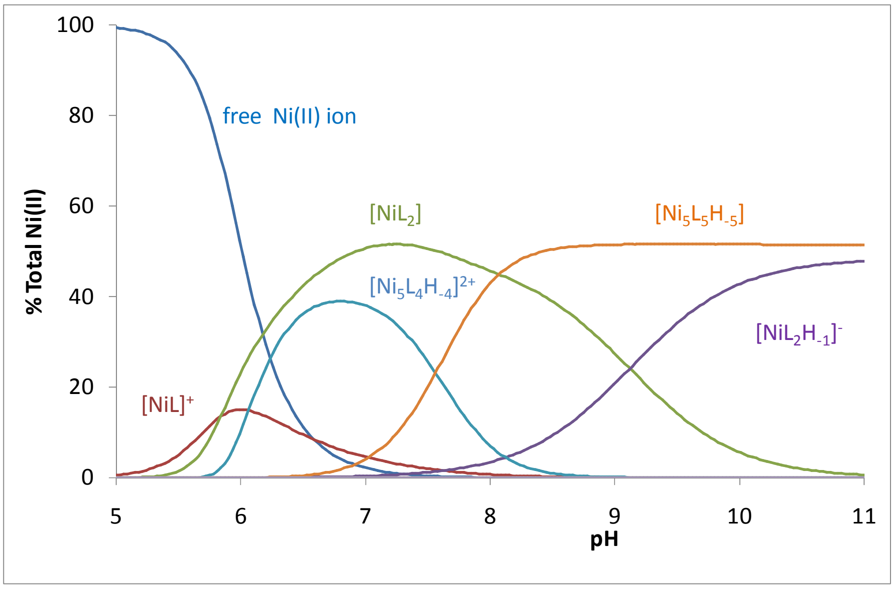


Figure S3 Exemplificative distribution diagram for the system Ni^{2+}/Valha with ligand-to-metal ratio 1:1.5 and $C°_{Ni}$ = 2 mmol dm^{-3}

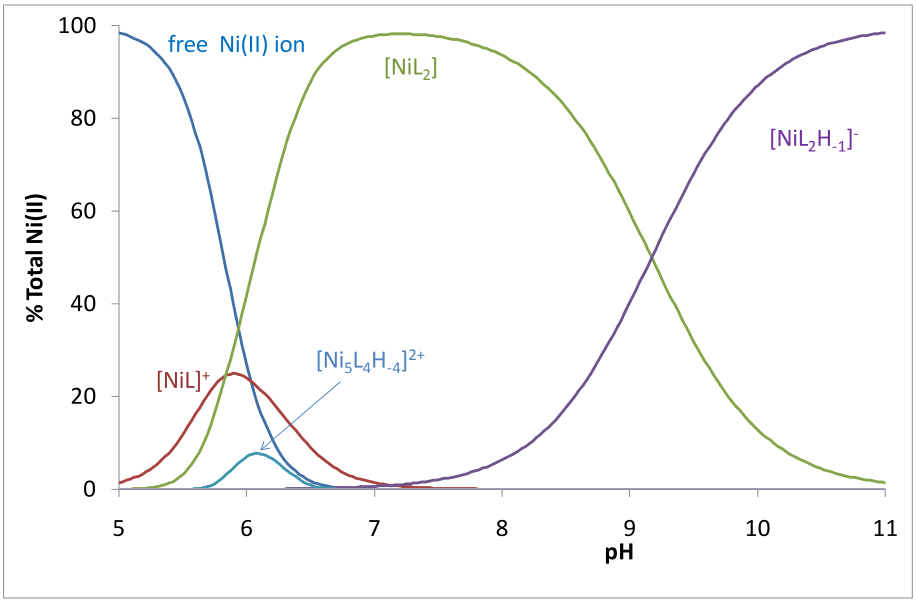
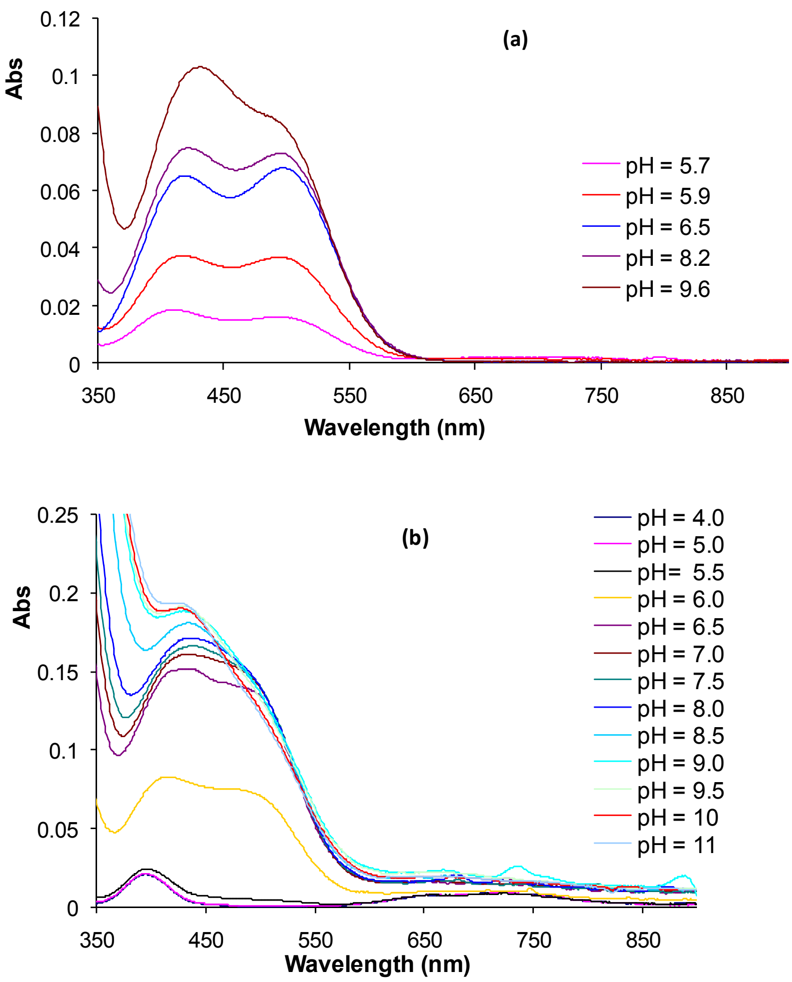


Figure S4 Exemplificative distribution diagram for the system Ni^{2+}/α-Alaha with ligand-to-metal ratio 1:3 and $C°_{Ni}$ = 2 mmol dm^{-3}

Table S3. Literature values for formation constants of Ni^{2+} and Cu^{2+} ML complexes with different chelating bidentate ligands [L. D. Pettit and H. K. J. Powell, in *Academic Software and IUPAC*, Royal Society of Chemistry, London, 1992-2000]

		Ni^{2+}			Cu^{2+}		
Ligand	Binding mode	log β	$-\Delta H°$ kJ mol^{-1}	$\Delta S°$ J K^{-1} mol^{-1}	log β	$-\Delta H°$ kJ mol^{-1}	$\Delta S°$ J K^{-1} mol^{-1}
Acha	{O, O}	5.15	-	-	7.85	13.5	105
glycine	{N, O}	6.12	18.6	55	8.50	25.9	76
ethylenediamine	{N, N}	7.54	37.7	18	10.60	52.5	27

Figure S5. Vis absorption spectra for the system Ni^{2+}/α-Alaha as a function of pH. a) ligand/metal ratio 8:1, $C°_{Ni}$ = 1 mM; b) ligand/metal ratio 1:1 $C°_{Ni}$ = 3 mmol dm^{-3}.



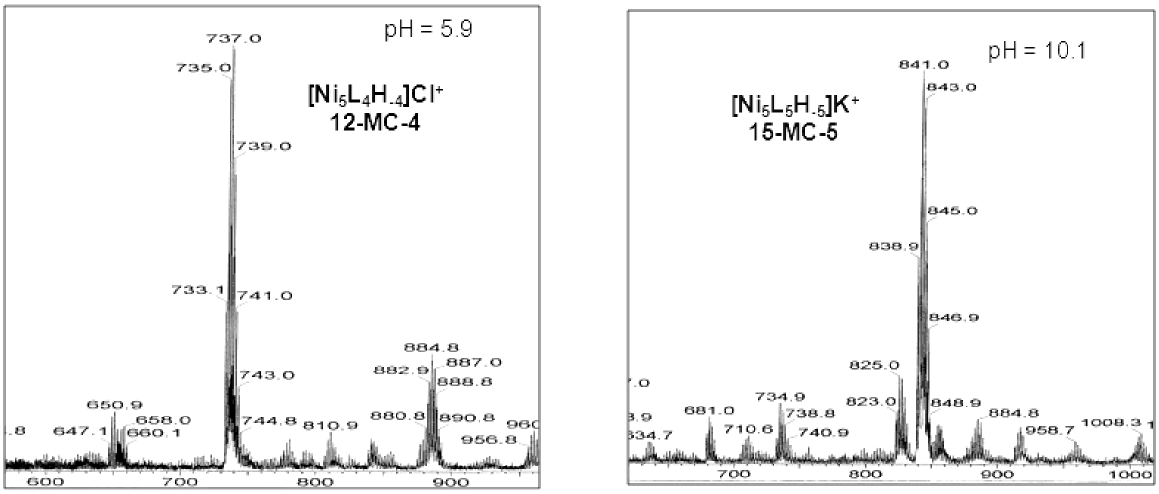


Figure S6. ESI-MS spectra for the Ni^{2+} / α-Alaha system in aqueous solution at pH 5.9 and 10.1, respectively. Base cation: K^+.

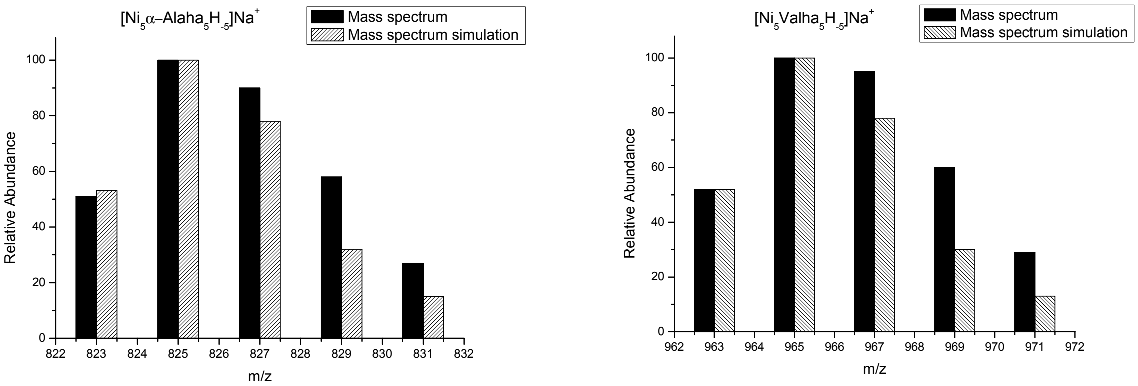


Figure S7. Comparison between experimental and calculated isotopic distributions for Ni(II) 15-MC-5 with α-Alaha and Valha.

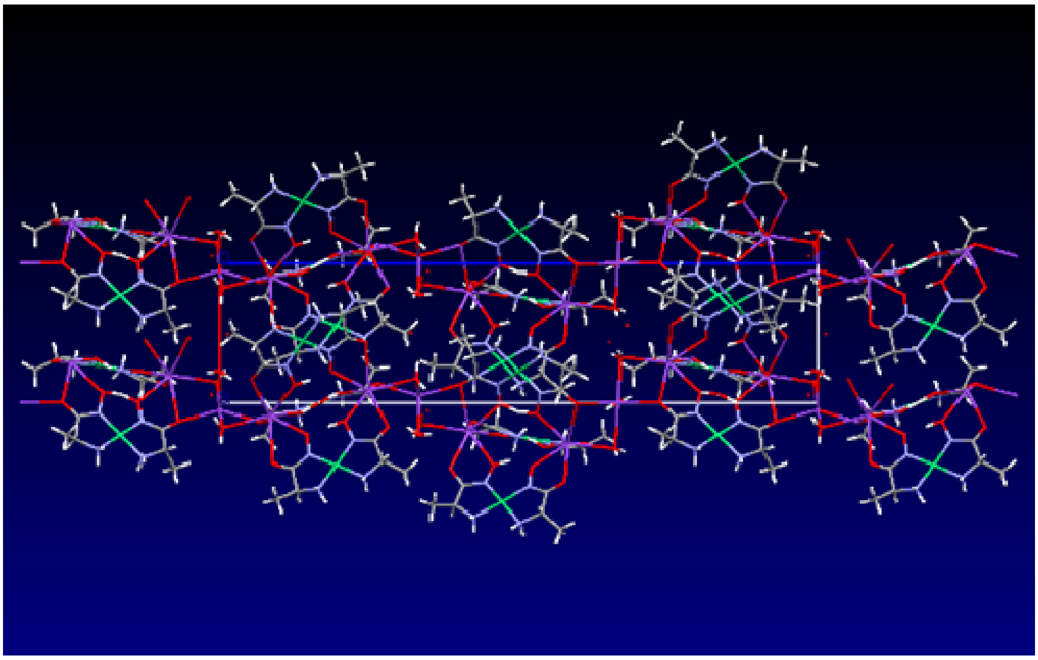


Figure S8. Unit cell packing viewed down the crystallographic *b* axis.