Electronic Supplementary Information

A comparative study on the nickel binding ability of peptides containing separate cysteinyl residues

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Table S1. Characteristic ^{1}H NMR spectral parameters (ppm) of the SSCSSACS-NH_2 ligand and equimolar nickel(II) containing system (pH = 10.1)

Ala (6), H_β			**Cys (3),(7) H_β**		
SSCSSACS-NH_2	Ni(II)–SSCSSACS*		SSCSSACS-NH_2	Ni(II)–SSCSSACS-NH_2*	
1.42	1.42	1.30	2.85	2.82	2.38
1.43	1.43	1.32	2.86	2.83	2.39
			2.88	2.85	2.41
			2.89	2.86	2.42
			2.90	2.88	3.02
			2.91	2.89	3.05
			2.92	2.91	3.06
			2.93	2.93	3.08
					3.29
					3.31
					3.33
					3.34

* The peaks detected in the Ni(II) containing system can be devided to two groups: one group corresponds to that of free ligand and the other group of peaks belongs to the nickel(II) complex

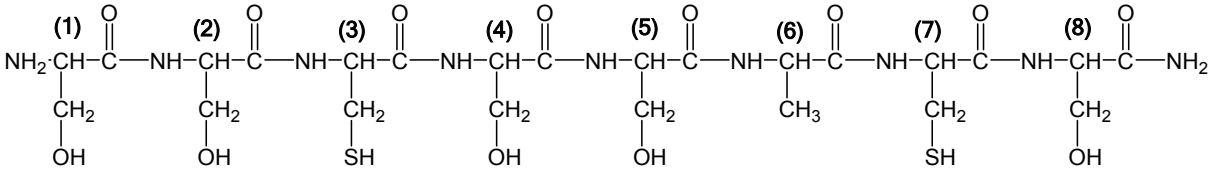
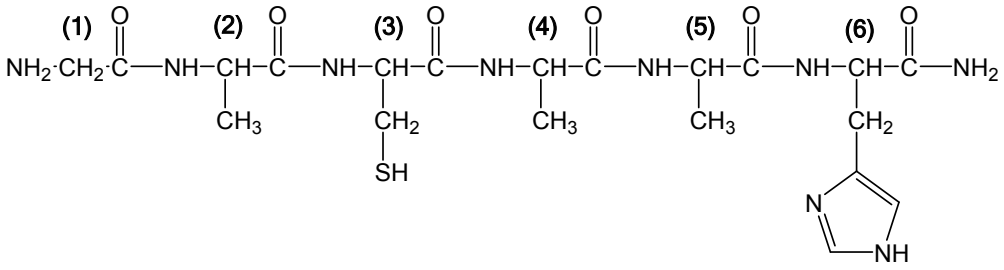
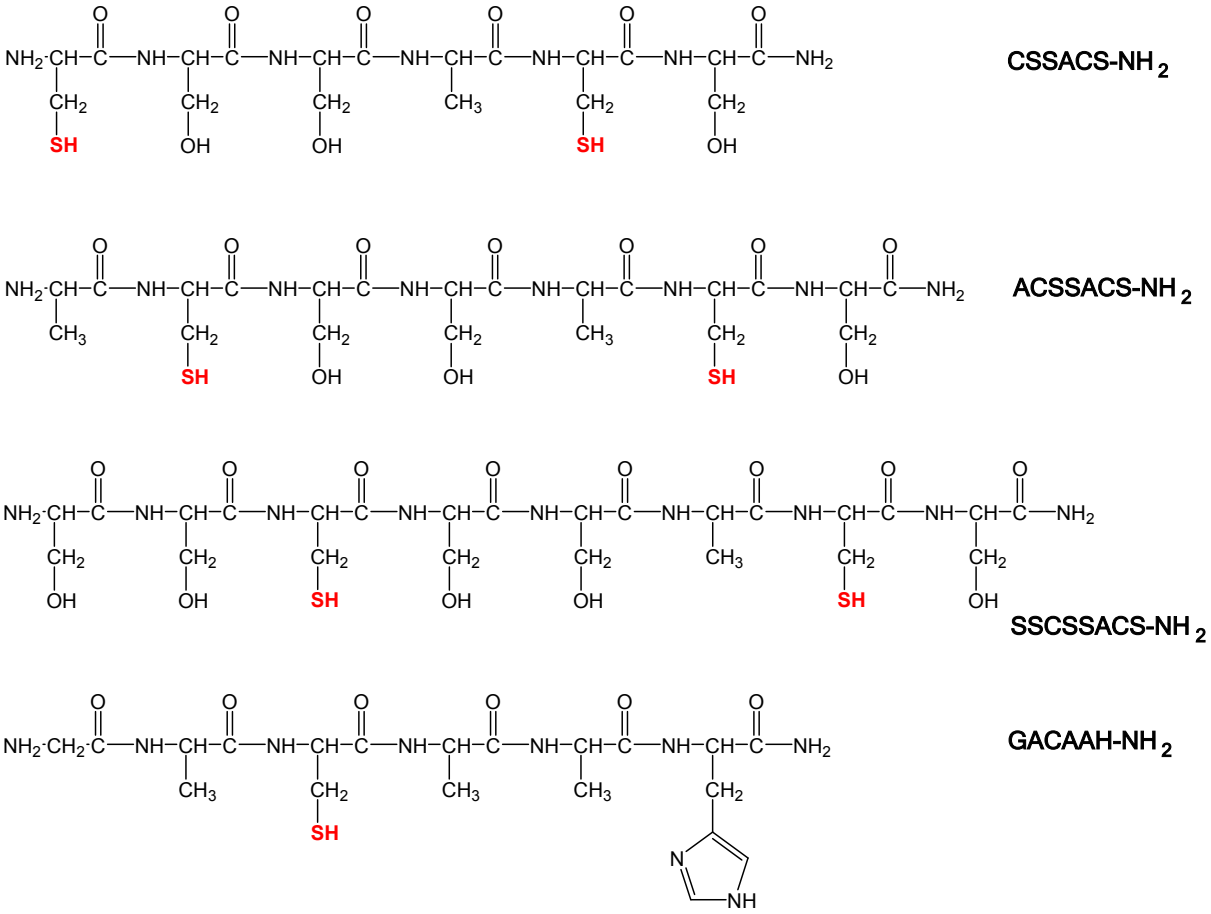


Table S2. Characteristic ^{1}H NMR spectral parameters (ppm) of the GACAAH-NH_2 ligand and equimolar nickel(II) containing system (pH = 10.0)

His (6), H_δ, H_ε		**Cys (3), H_β**		**Cys (3) H_α**	
GACAAH-NH_2	Ni(II)–GACAAH-NH_2	GACAAH-NH_2	Ni(II)–GACAAH-NH_2	GACAAH-NH_2	Ni(II)–GACAAH-NH_2
7.71, 6.98	7.69, 7.00	2.87	2.38	4.36	2.75
		2.89	2.41	4.38	2.77
				4.40	2.78





Scheme S1. Structural formulas of the investigated ligands

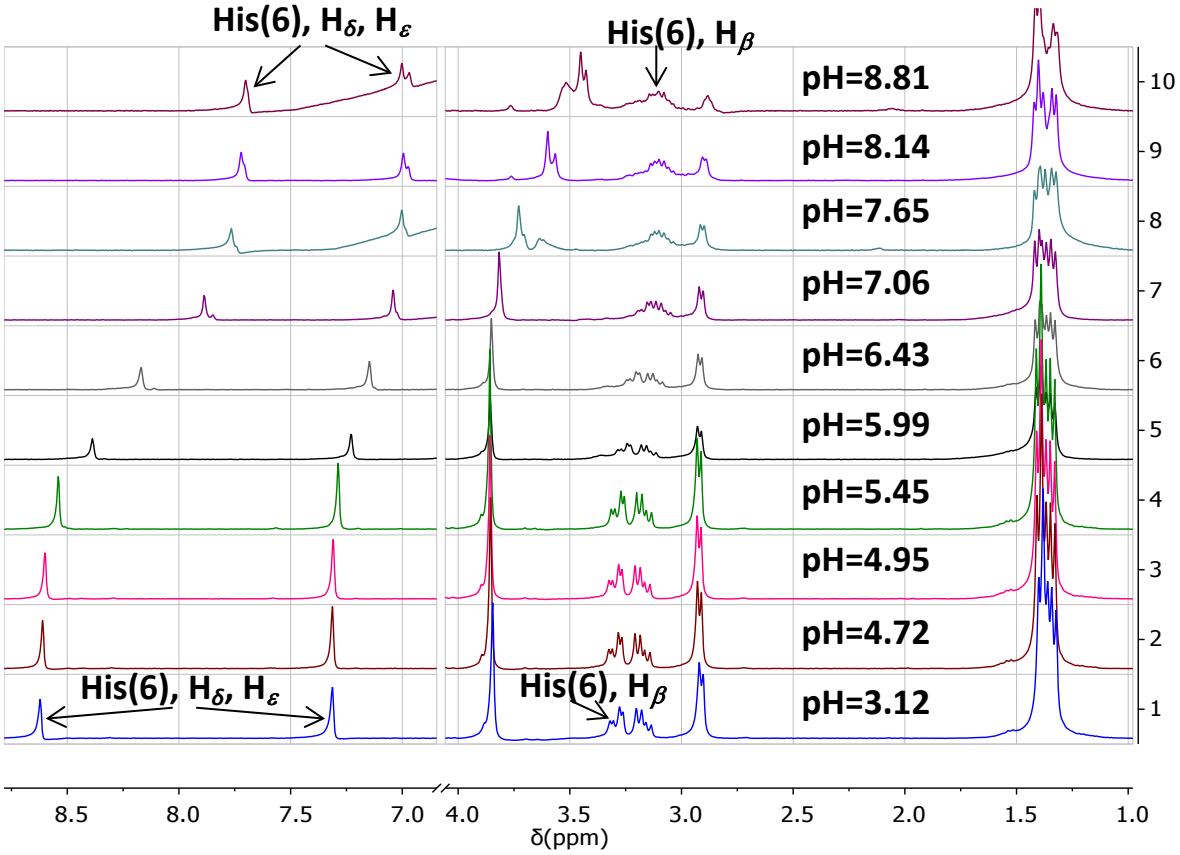
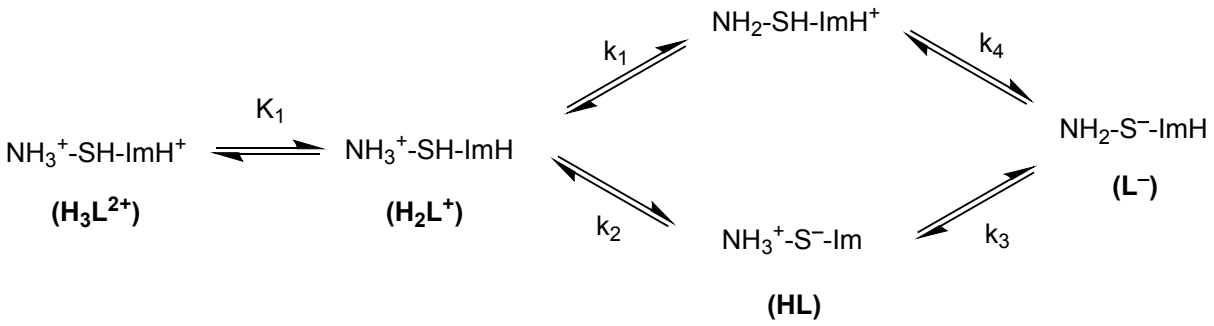
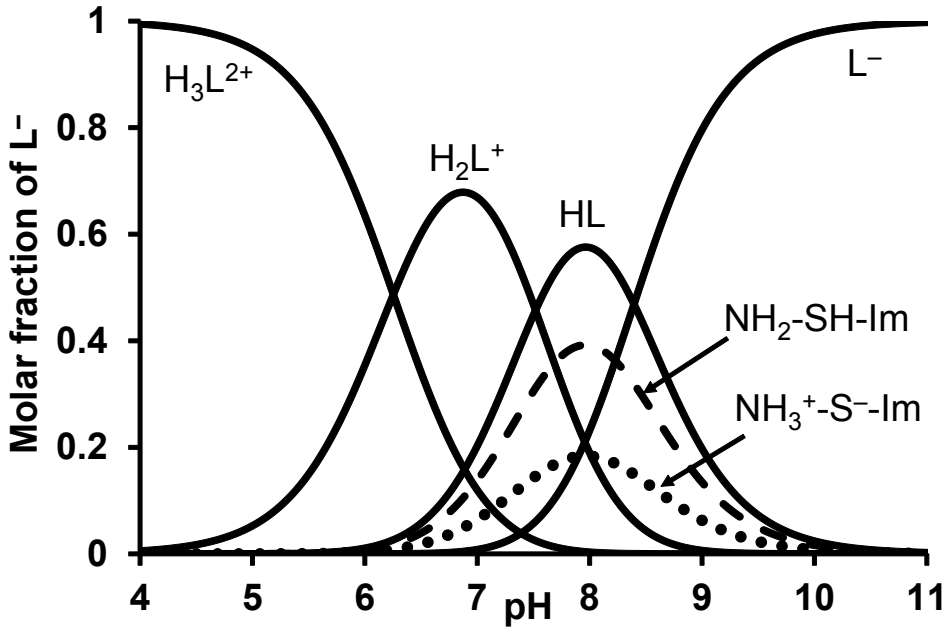


Figure S1. pH-dependent ^{1}H NMR spectra of GACAAH-NH_2 (c_L = 2 mM)



(a)



(b)

Figure S2. Protonation scheme (a) and speciation curves (b) for the peptide GACAAH-NH_2

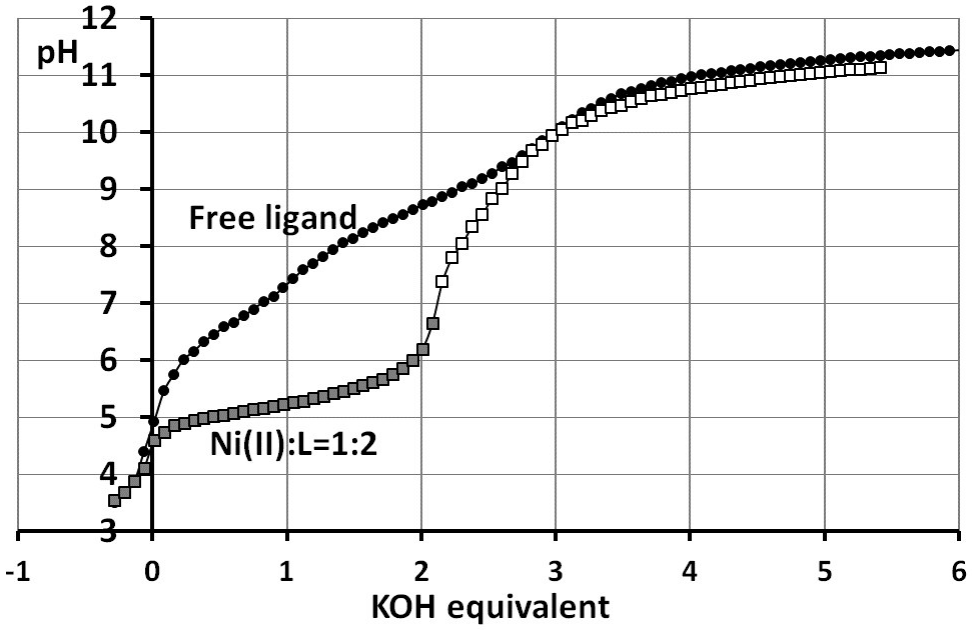


Figure S3. Titration curves of CSSACS-NH_2 (c_L = 1.137 mM) and Ni(II)-CSSACS-NH_2 system at 1:2 ratio (c_L = 1.137 mM, c_M = 0.555 mM) (the empty squares sign the precipation)

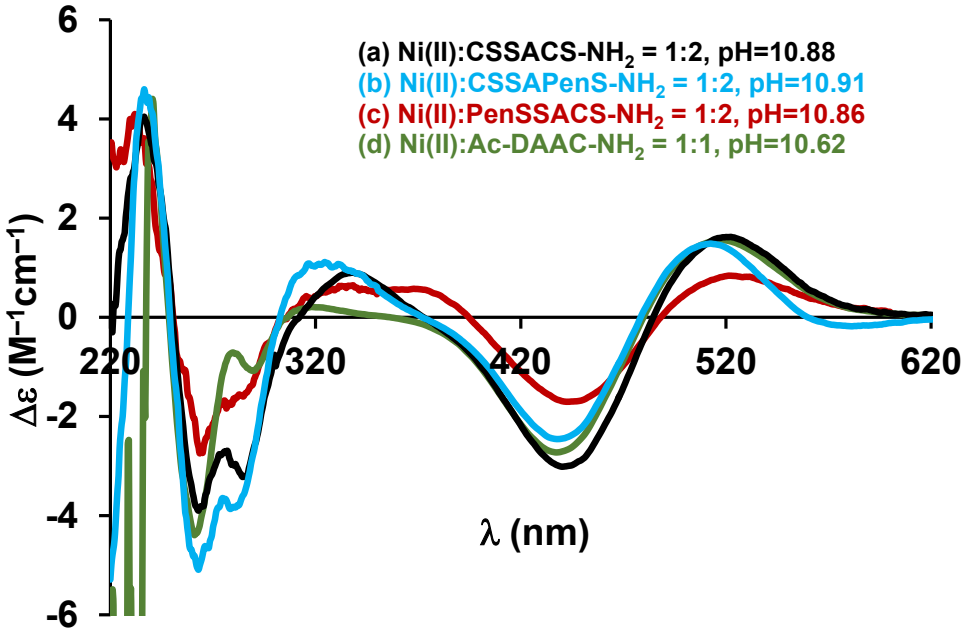


Figure S4. CD spectra of nickel(II) complexes of thiol containing peptides ((b) and (c) spectra from ref. 27, (d) spectrum from ref. 21)

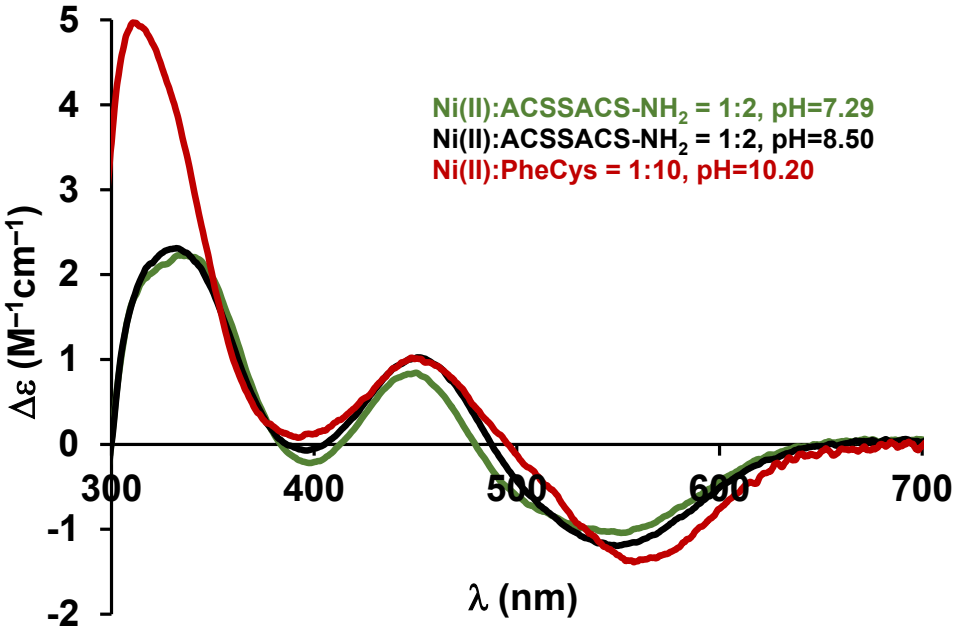


Figure S5. CD spectra of the bis(ligand) complexes formed in the Ni(II)-ACSSACS-NH_2 and Ni(II)-PheCys systems

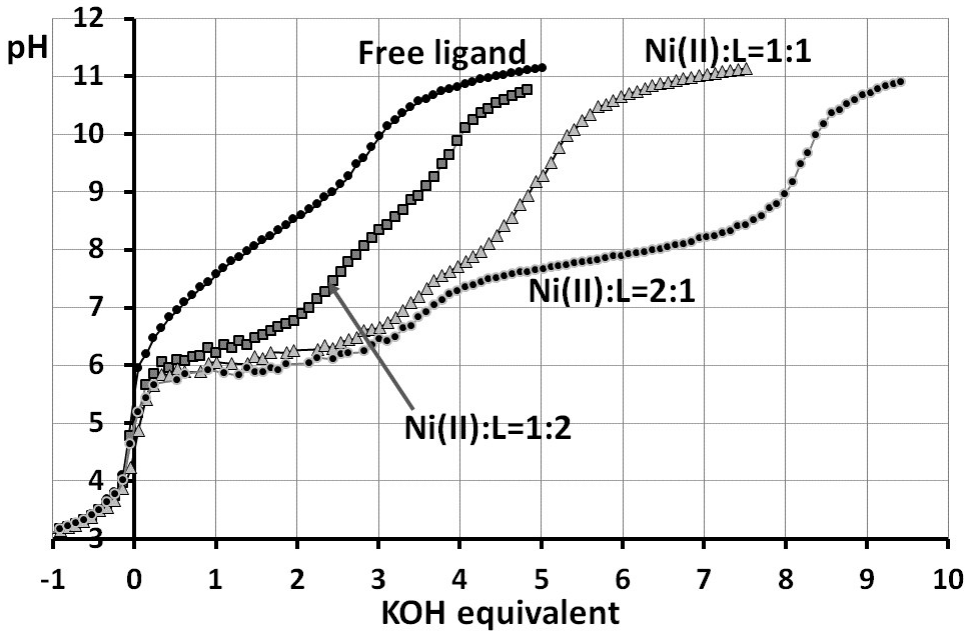
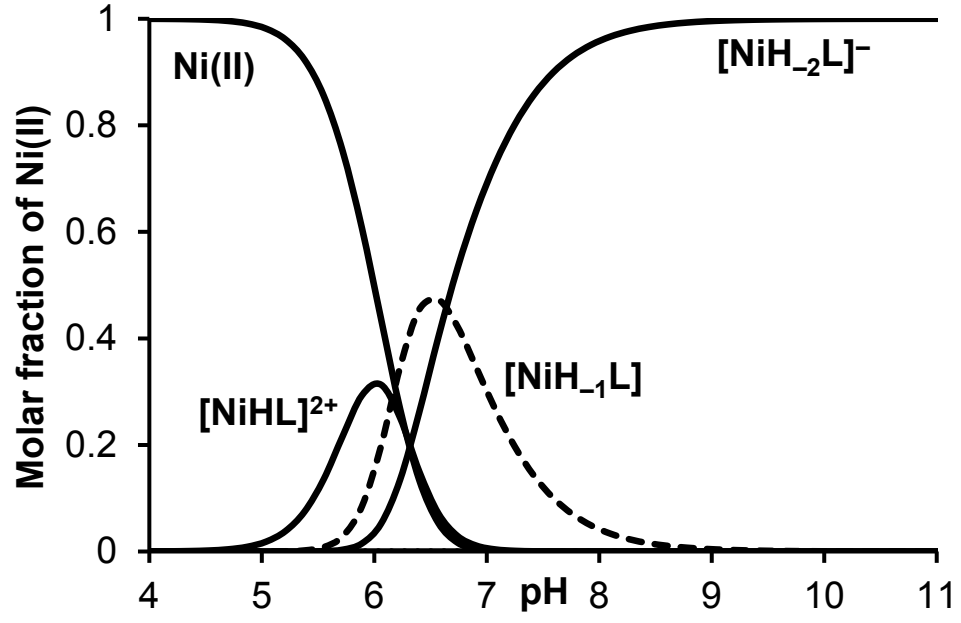
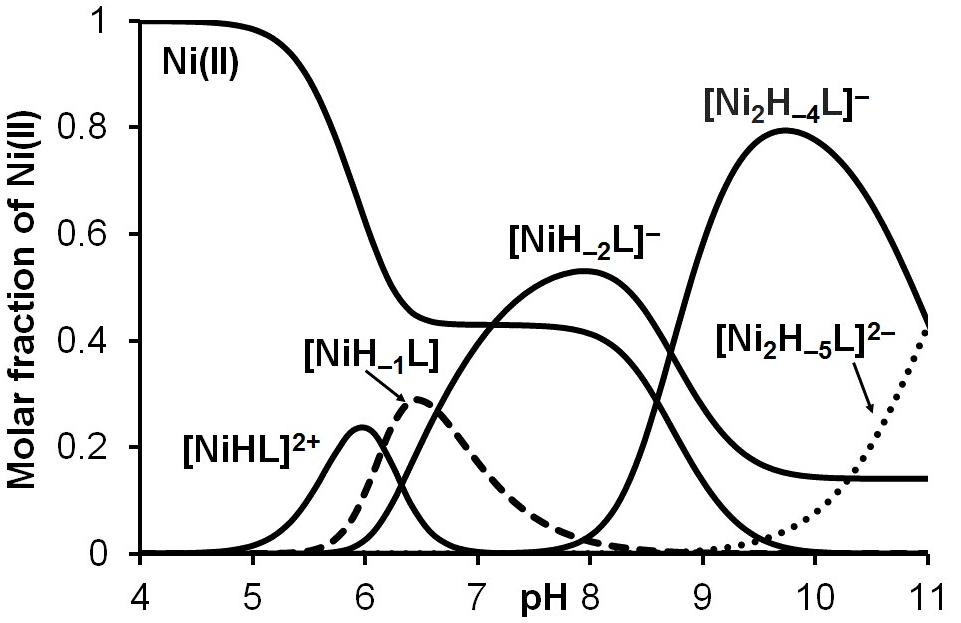


Figure S6. Titration curves of SSCSSACS-NH_2 (c_L = 0.933 mM) and Ni(II)-SSCSSACS-NH_2 system at different ratios (c_L = 0.933 mM, c_M = 0.451 mM, (1:2), c_M = 0.902 mM, (1:1), c_M = 1,838 mM, (2:1))



(a)



(b)

Figure S7. Species distribution of the Ni(II)-GACAAH-NH_2 system at 1:1 (a) and 2:1 (b) metal to ligand ratios (c_L = 2 mM)

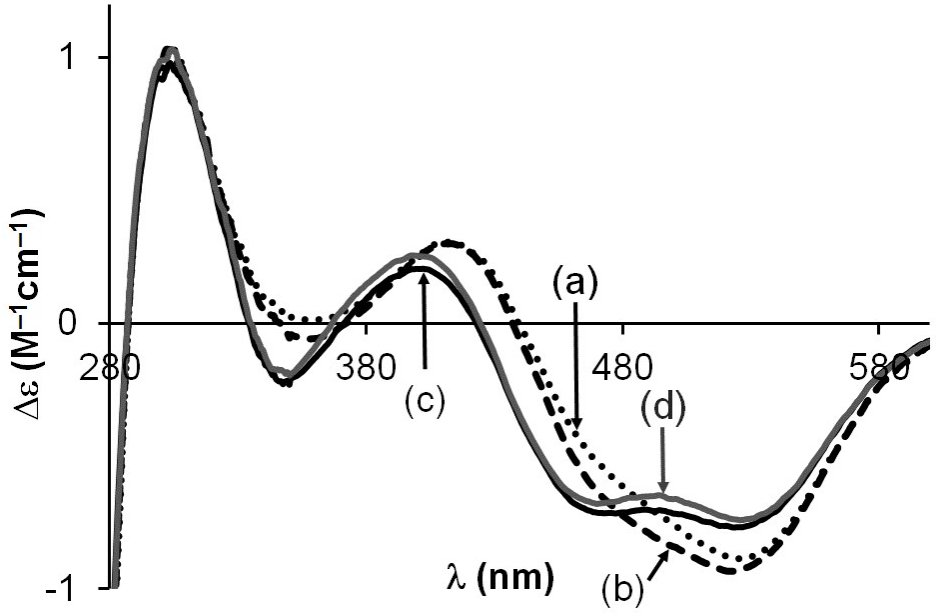


Figure S8. CD spectra recorded in the Ni(II)-GACAAH-NH_2 system at 2:1 in the function of pH: pH = 6.55 (a) (•••); pH = 8.10 (b) (– – –); pH = 9.59 (c) (—); pH = 10.56 (d) (—)

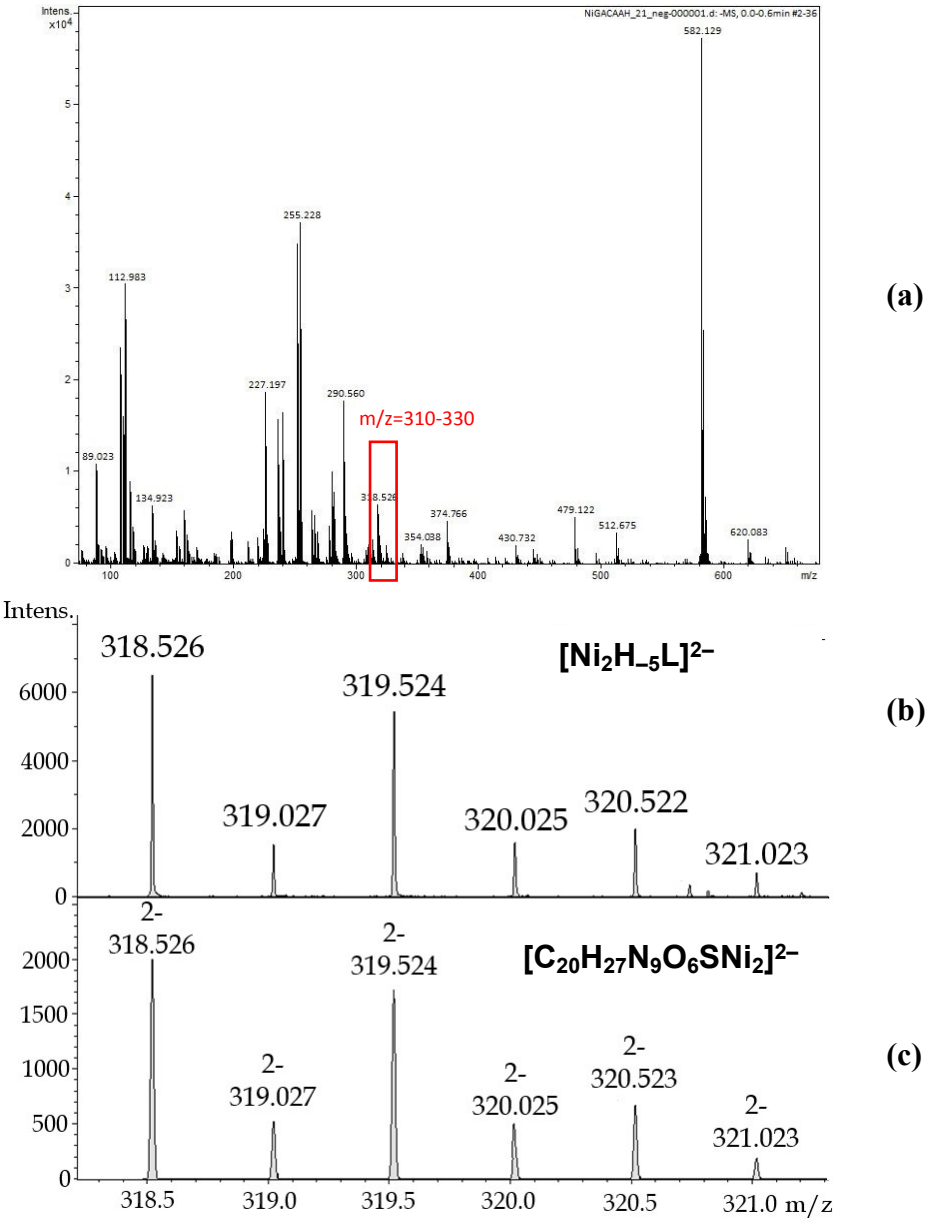
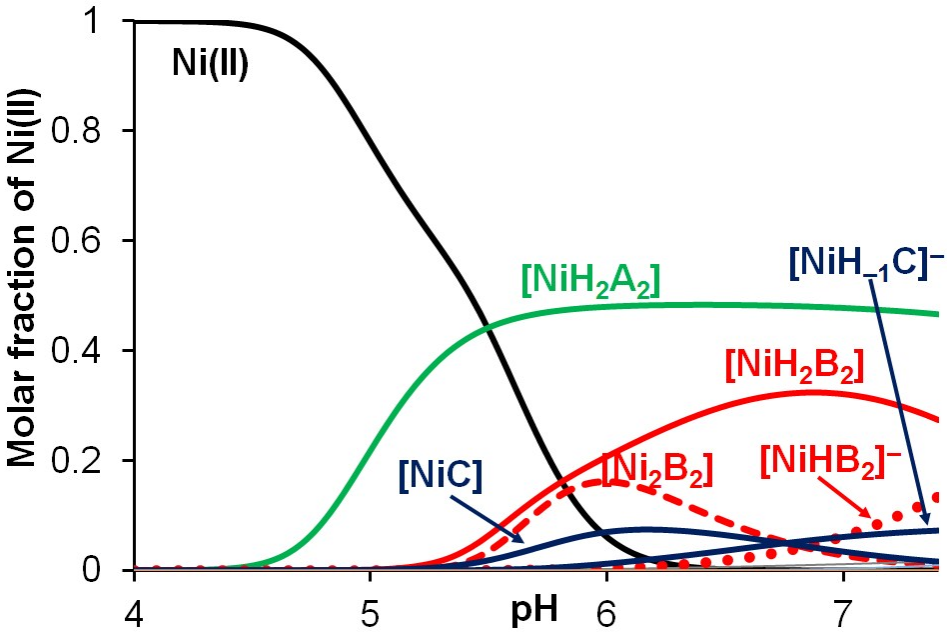
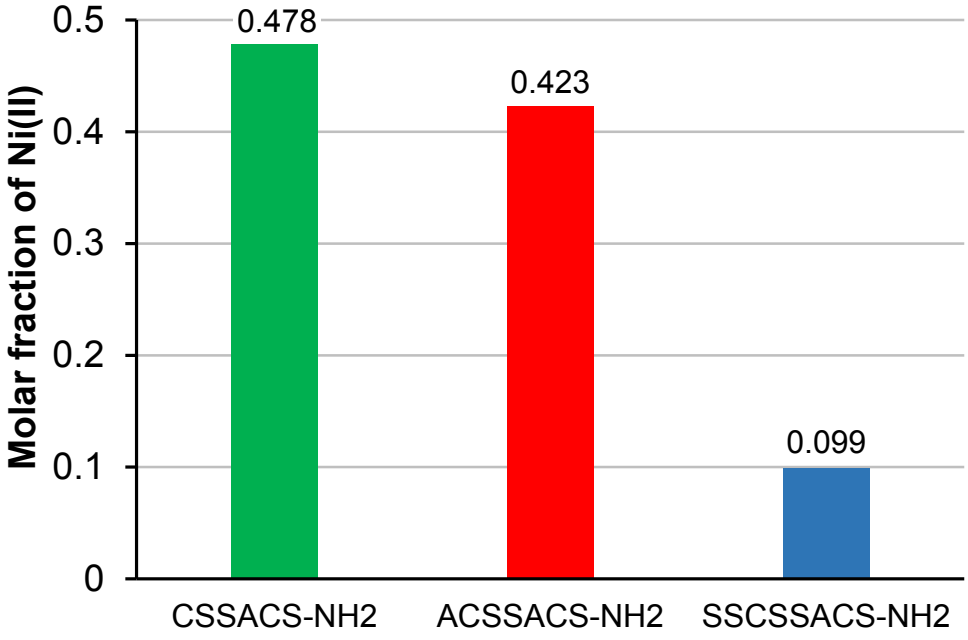


Figure S9 ESI-MS spectra of the Ni(II)-GACAAH-NH_2 2:1 sample (a), measured isotopic profiles (b) and theoretical isotopic patterns (c) of $[Ni_2H_{-5}L]^{2-}$ dinuclear complex of GACAAH-NH_2.



(a)



(b)

Figure S10 (a) Concentration distribution of the complexes formed with the peptides CSSACS-NH_2 (A), ACSSACS-NH_2 (B) and SSCSSACS-NH_2 (C) in a model system containing all components in the same concentration (c = 1 mM)

(b) Ratio of the nickel(II) complexes at pH 7.0 formed with the peptides CSSACS-NH_2, ACSSACS-NH_2 and SSCSSACS-NH_2 in a model system containing all components in the same concentration (c = 1 mM)

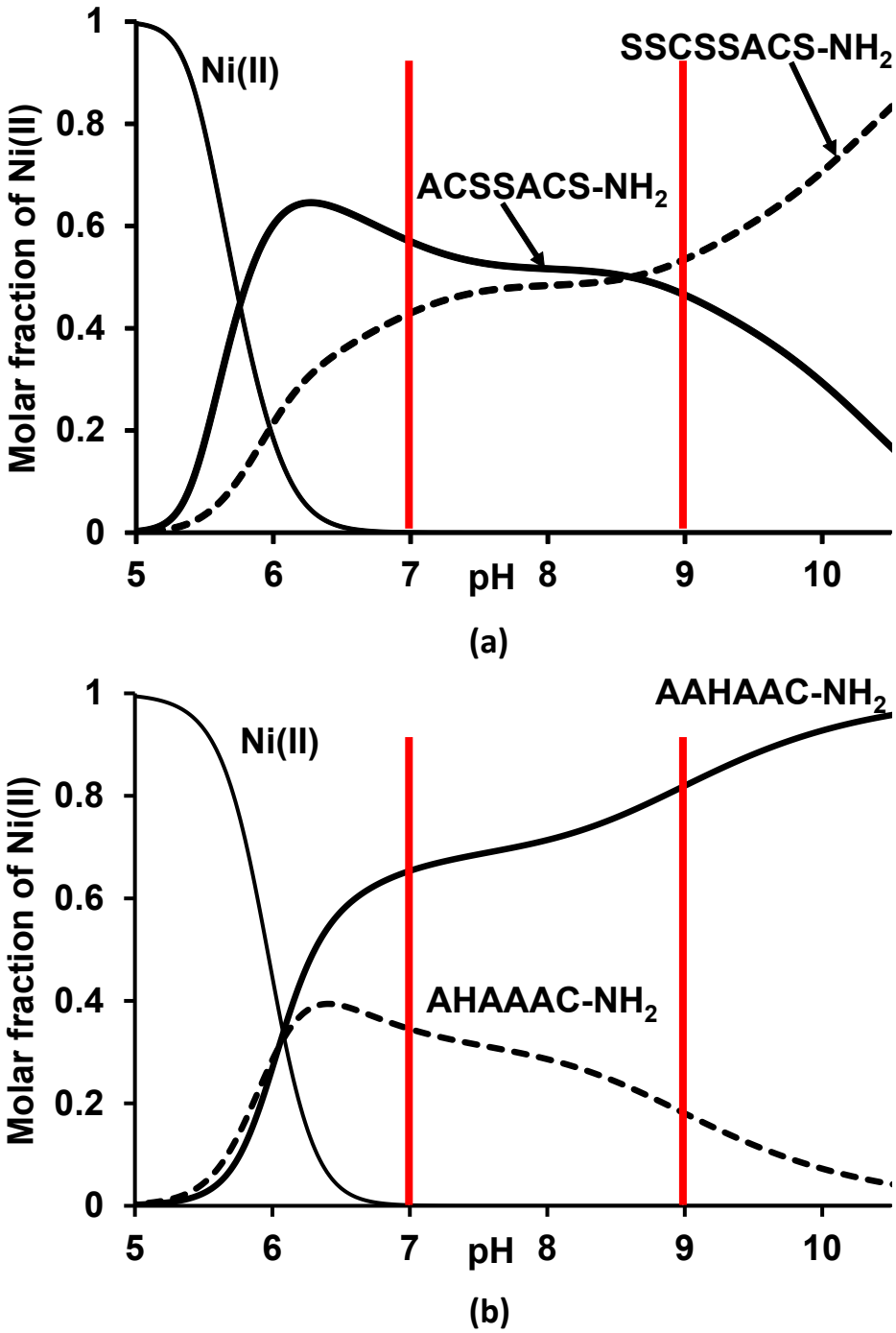


Figure S11 Distribution of nickel(II) among the peptides ACSSACS-NH_2 and SSCSSACS-NH_2 (a) and AHAAAC-NH_2 and AAHAAC-NH_2 (b) in a model system containing all components in the same concentration (c = 1 mM)