Electronic Supplementary Information in New Journal of Chemistry

The effect of side chains on the complex formation processes of N-terminally free hexapeptides containing C-terminal cysteinyl functions

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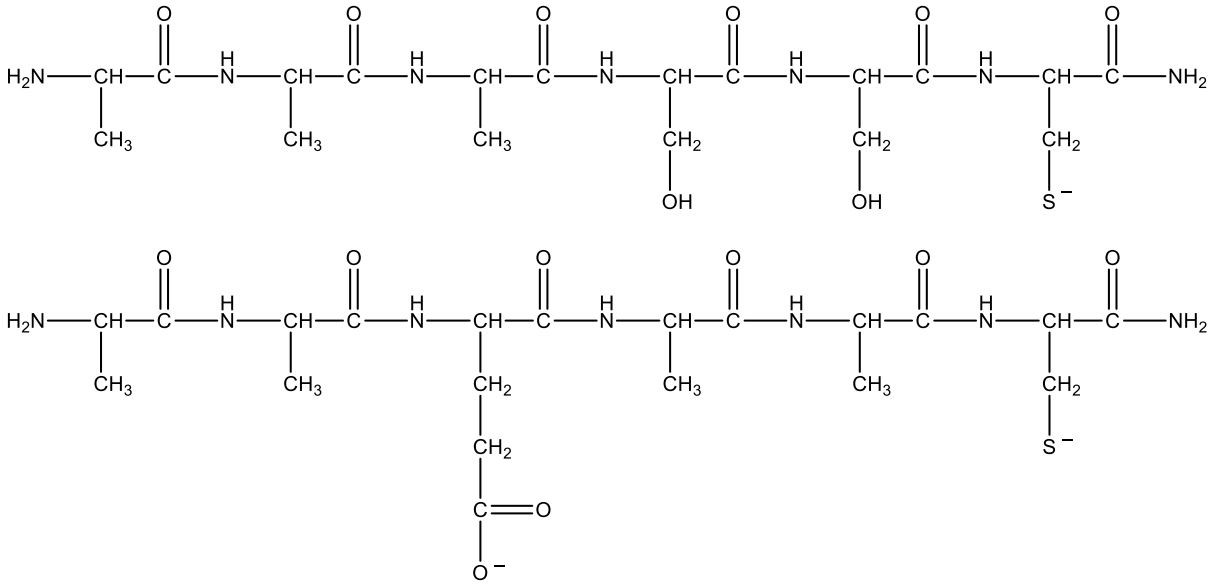
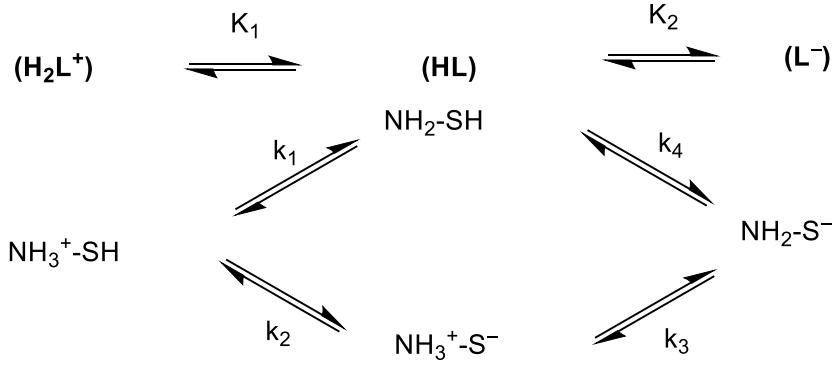
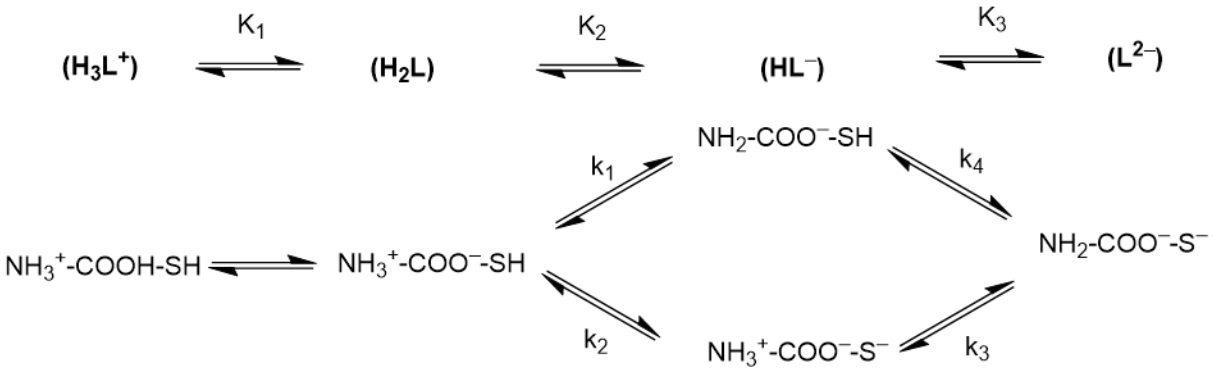


Scheme S1 Structure of the investigated ligands AAASSC-NH_2 and AAEAAC-NH_2 (deprotonated forms)



Scheme S2 Dissociation processes of AAASSC-NH_2



Scheme S3 Dissociation processes of AAEAAC-NH_2

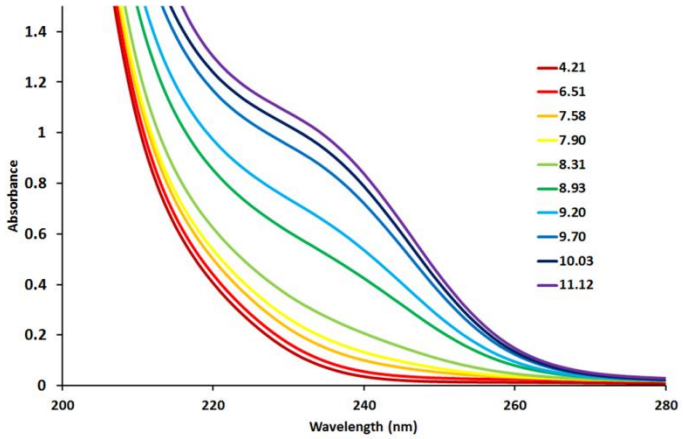


Figure S1 UV-absorption spectra of the ligand AAEAAC-NH_2 depending on pH (c_L = 5 mM)

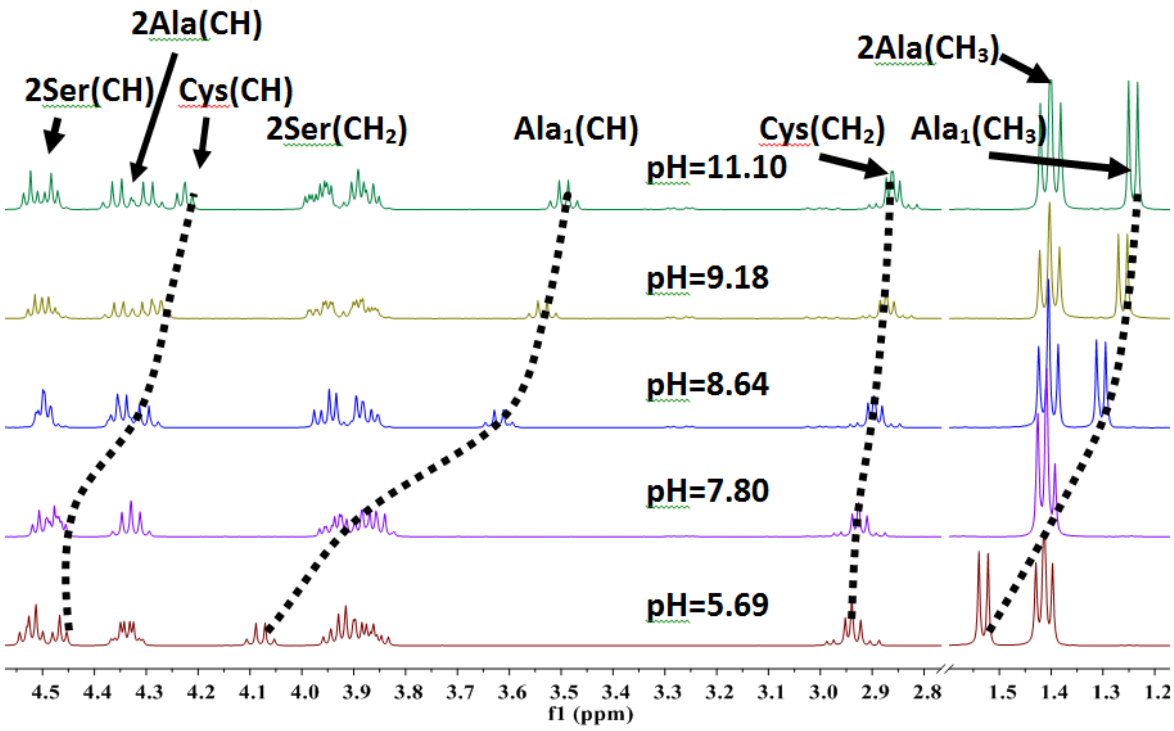
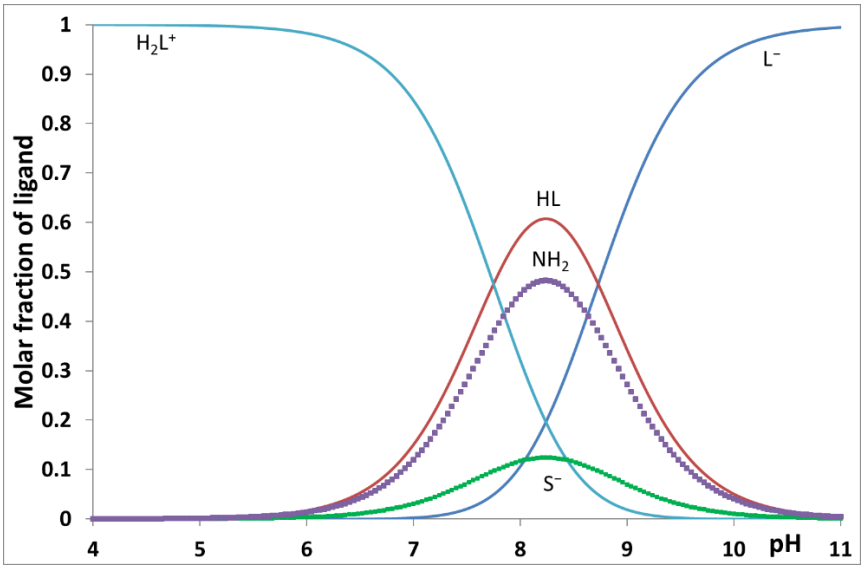
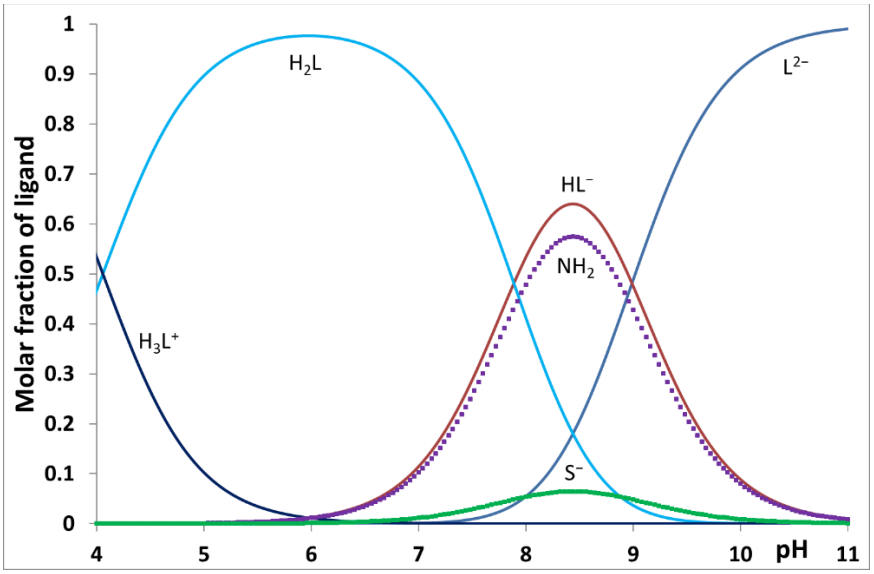


Figure S2 ^{1}H NMR spectra (c_L = 5 mM) (b) of the ligand AAASSC-NH_2 depending on pH



(a)



(b)

Figure S3 Distribution of microspecies as a function of pH for AAASSC-NH_2 (a) and AAEAAC-NH_2 (b)

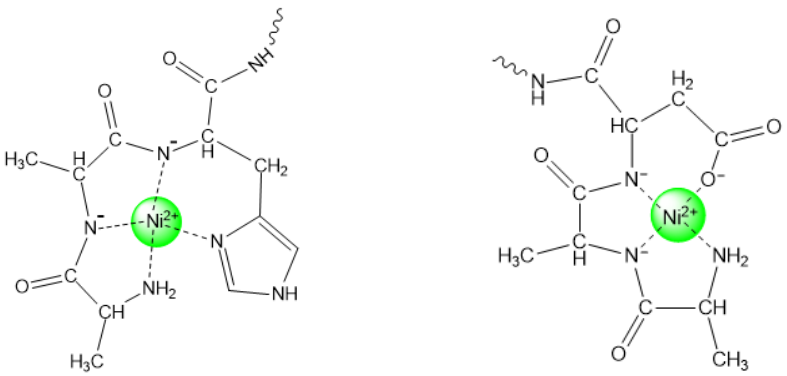


Figure S4 Supposed structures of the $NiH_{-1}L$ complexes of AAHAAC-NH_2 with the (NH_2, N^-, N^-, N_{Im}) (left) and AADAAC-NH_2 with the (NH_2, N^-, N^-, β-COO^-) (right) binding mode.

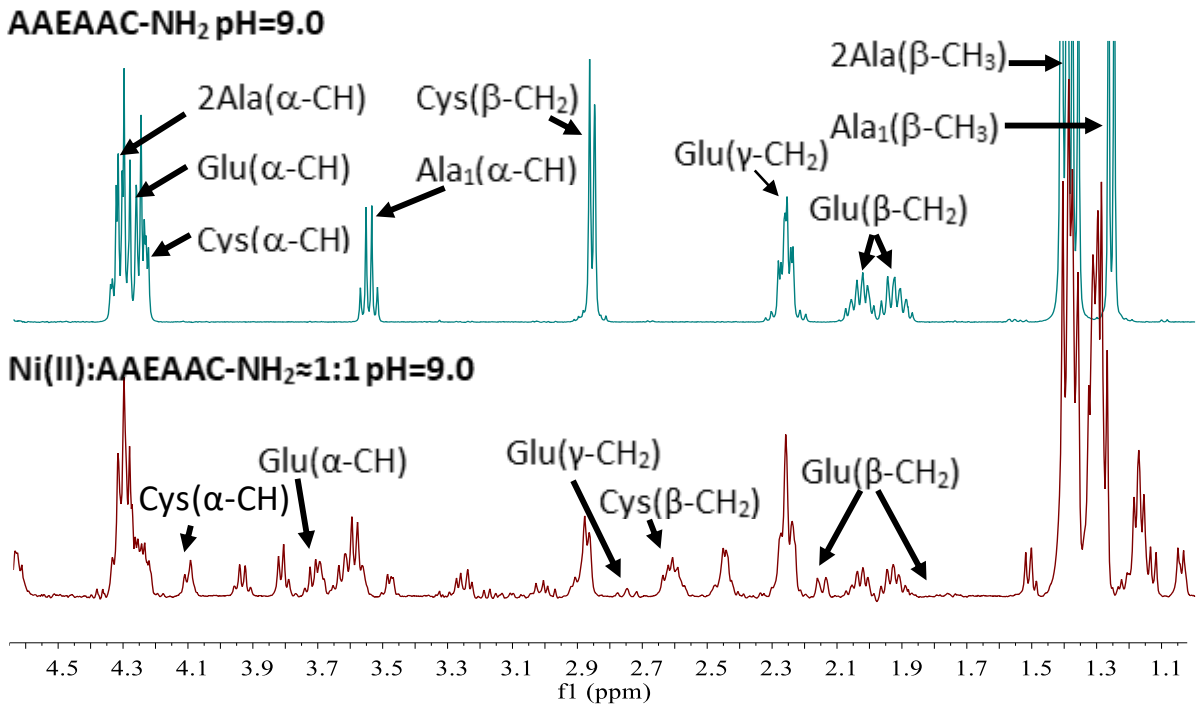


Figure S5 ^{1}H NMR spectra of the free ligand AAEAAC-NH_2 and in the presence of equimolar nickel(II) at pH=9 (c_L= $c_{Ni^{2+}}$ = 5 mM)

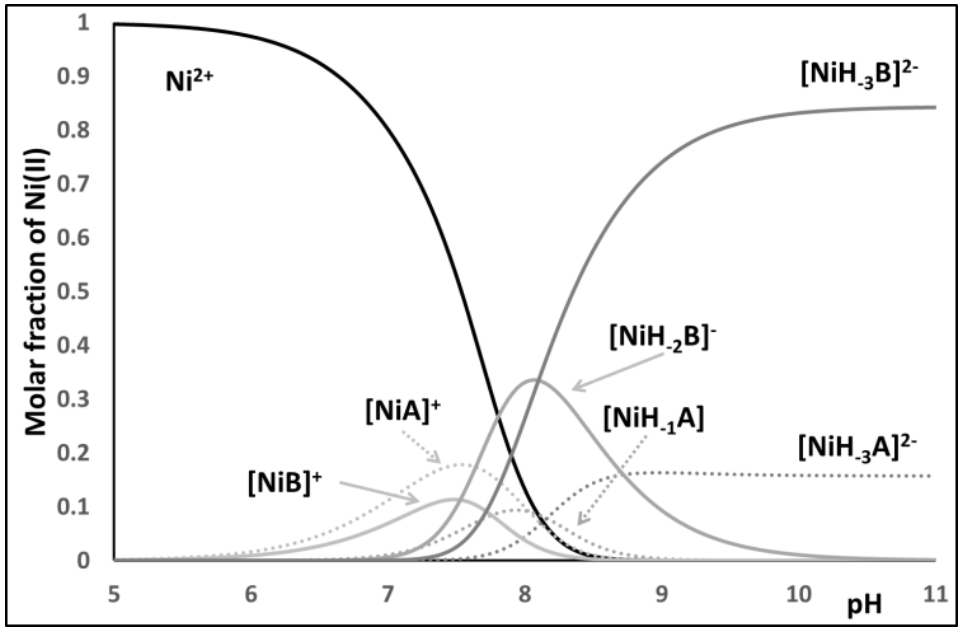


Figure S6 Hypothetic distribution of nickel(II) complexes formed in the Ni(II) : AAAA : Ac-AAAC-NH_2 = 1:1:1 (c = 2 mM) (data from ref. [32] (AAAA – **A**) and [33] (Ac-AAAC-NH_2 - **B**))

Table S1 Relative energy values in gas phase and in water simulated by SMD for the formation of coordination isomers in the $NiH_{-3}L$ complexes.[a]

	ΔE^{ele}	ΔG^{therm}	ΔG^{tot}_{gas}	$\Delta(\Delta G^{solv})$	ΔG^{tot}_{aq}
$NiH_{-3}L$ (NH_2,N^-, N^-, N^-) → $NiH_{-3}L$ (N^-,N^-, N^-, S^-) L: AAASSC-NH_2	-28.4	-26.2	5.7	-36.8	-31.1
$NiH_{-3}L$ (NH_2,N^-, N^-, N^-) → $NiH_{-3}L$ (N^-,N^-, N^-, S^-) L: AAEAAC-NH_2	0.7	2.2	101.1	-97.4	3.7

[a] Values are reported in kJ/mol. Thermal contribution at 298 K and zero-point energies are included in the calculations.

Table S2 Energies and Cartesian coordinates of the $NiH_{-3}L$ complex with (NH_2,N^-,N^-,N^-) donors in gas phase. L refers to AAASSC-NH_2.

Sum of electronic and zero-point Energies (Eh)	-3600.917041
Sum of electronic and thermal Energies (Eh)	-3600.879962
Sum of electronic and enthalpy Energies (Eh)	-3600.879018
Sum of electronic and thermal Free Energies (Eh)	-3600.990706
Number of Imaginary Frequencies	0

Molecular Geometry in Cartesian Coordinates

N	2.376047	1.835521	-0.441330
H	1.576140	1.870711	-1.064424
C	3.366886	2.886093	-0.781786
H	3.357010	2.979430	-1.871983
C	3.047587	4.230503	-0.161664
C	4.788486	2.410618	-0.426139
H	2.103904	4.637643	-0.533625
H	2.982103	4.143622	0.926874
H	3.857086	4.923548	-0.389801
O	5.730609	3.210823	-0.507226
N	4.807361	1.129507	-0.110127
C	6.027601	0.393077	0.141112
H	6.740702	0.563168	-0.675551
C	6.703193	0.780029	1.450543
C	5.677299	-1.103464	0.153190
H	6.006097	0.645923	2.281594
H	7.568142	0.135498	1.616017
H	7.017649	1.823616	1.417330
O	6.555581	-1.962921	0.289684
N	4.366145	-1.310126	0.028388
C	3.745951	-2.608544	0.069971
H	4.181549	-3.268125	-0.692674
C	3.881961	-3.293457	1.425002
C	2.263019	-2.440448	-0.279025
H	3.458078	-2.656108	2.204493
H	3.333225	-4.236341	1.411940
H	4.934370	-3.472805	1.644079
O	1.526900	-3.429314	-0.321165
N	1.914574	-1.164233	-0.523139
C	0.556172	-0.841242	-0.868890
H	0.583655	0.061492	-1.492982
C	-0.196306	-1.852807	-1.774653
C	-0.319798	-0.493392	0.338978

H	0.528769	-2.255403	-2.482102
H	-0.584624	-2.686843	-1.193453
O	-1.219408	-1.205626	-2.522930
O	-0.072530	-0.783526	1.492598
H	-2.078436	-1.318942	-2.083676
N	-1.459146	0.182807	-0.012511
H	-1.668476	0.192502	-1.003093
C	-2.605707	0.174521	0.854866
H	-2.436508	-0.608275	1.606695
C	-2.742504	1.501077	1.607141
C	-3.843877	-0.212888	0.028371
H	-1.738068	1.823230	1.897481
H	-3.190365	2.262495	0.966798
O	-3.589010	1.402220	2.745716
O	-3.715040	-0.729286	-1.079412
H	-3.203781	0.746303	3.336284
N	-5.016008	0.036177	0.616846
H	-4.983349	0.569288	1.476689
C	-6.299638	-0.065914	-0.045518
H	-6.189384	-0.760196	-0.879175
C	-7.358395	-0.631524	0.923993
C	-6.680185	1.315086	-0.601856
H	-6.890834	-1.498969	1.398314
H	-7.521233	0.111253	1.717212
S	-8.936834	-1.128872	0.173290
O	-5.967493	2.300945	-0.450579
N	-7.852878	1.321821	-1.259994
H	-8.222249	2.236918	-1.468624
H	-8.504484	0.531728	-1.023141
H	2.013080	1.992984	0.496003
Ni	3.283556	0.108637	-0.282085

Table S3 Energies and Cartesian coordinates of the $NiH_{-3}L$ complex with (NH_2,N^-,N^-,N^-) donors in water. L refers to AAASSC-NH_2.

Sum of electronic and zero-point Energies (Eh)	-3601.164824
Sum of electronic and thermal Energies (Eh)	-3601.128015
Sum of electronic and enthalpy Energies (Eh)	-3601.127071
Sum of electronic and thermal Free Energies (Eh)	-3601.235679
Number of Imaginary Frequencies	0

Molecular Geometry in Cartesian Coordinates

N	2.554974	1.891612	-0.528360
H	1.860403	1.966520	-1.264961
C	3.653081	2.857548	-0.792286
H	3.699247	2.994091	-1.876151
C	3.409423	4.197427	-0.130748
C	4.988455	2.235220	-0.403829
H	2.483341	4.643090	-0.497076
H	3.335662	4.084760	0.953798
H	4.227797	4.882762	-0.350857
O	6.043297	2.906474	-0.484544
N	4.882545	0.970148	-0.056181
C	6.029260	0.123276	0.214014
H	6.779079	0.243131	-0.577207

C	6.692811	0.406411	1.555941
C	5.536694	-1.320680	0.174471
H	5.979742	0.273489	2.372705
H	7.528985	-0.276568	1.713429
H	7.073125	1.427247	1.590143
O	6.343706	-2.275815	0.260761
N	4.222472	-1.412902	0.064114
C	3.494788	-2.658341	0.067239
H	3.892316	-3.340546	-0.694741
C	3.531338	-3.364152	1.418529
C	2.049900	-2.350421	-0.313769
H	3.105219	-2.724274	2.194458
H	2.956745	-4.290232	1.379315
H	4.557004	-3.607543	1.694285
O	1.243444	-3.300281	-0.416773
N	1.788792	-1.055373	-0.493590
C	0.453103	-0.611890	-0.836126
H	0.550746	0.369208	-1.303441
C	-0.305818	-1.447465	-1.895878
C	-0.456477	-0.453531	0.373112
H	0.411335	-1.742276	-2.663240
H	-0.730937	-2.349400	-1.458006
O	-1.314721	-0.680049	-2.529876
O	-0.409265	-1.197457	1.349650
H	-2.090829	-0.635931	-1.932781
N	-1.363977	0.541414	0.255962
H	-1.372812	1.047806	-0.618435
C	-2.577109	0.573731	1.028311
H	-2.450415	-0.129735	1.855553
C	-2.802789	1.966258	1.625806
C	-3.743247	0.053730	0.177515
H	-1.866030	2.292449	2.082744
H	-3.068573	2.677826	0.842494
O	-3.855991	1.994965	2.575427
O	-3.549354	-0.526439	-0.899034
H	-3.576001	1.490987	3.349787
N	-4.955404	0.232245	0.694106
H	-5.020483	0.784090	1.544718
C	-6.185320	-0.234552	0.070859
H	-5.972023	-1.176208	-0.434260
C	-7.247755	-0.459491	1.138238
C	-6.657847	0.797981	-0.949987
H	-6.820552	-1.147996	1.873002
H	-7.406521	0.493937	1.653795
S	-8.808133	-1.107962	0.472072
O	-6.933599	1.951010	-0.605344
N	-6.703053	0.397323	-2.220231
H	-7.041157	1.027277	-2.931852
H	-6.509383	-0.559342	-2.465453
H	2.077938	2.151079	0.333116
Ni	3.272773	0.109314	-0.252121

Table S4 Energies and Cartesian coordinates of the $NiH_{-3}L$ complex with (N^-,N^-,N^-,S^-) donors in gas phase. L refers to AAASSC-NH_2.

Sum of electronic and zero-point Energies (Eh)	-3600.914123
Sum of electronic and thermal Energies (Eh)	-3600.876427
Sum of electronic and enthalpy Energies (Eh)	-3600.875483

Sum of electronic and thermal Free Energies (Eh) -3600.988525

Number of Imaginary Frequencies 0

Molecular Geometry in Cartesian Coordinates

N	9.849289	-1.152708	0.723385
H	9.569758	-2.129481	0.788266
C	8.657250	-0.363118	0.992576
H	8.568047	-0.255426	2.081605
C	8.804457	1.024071	0.390236
C	7.378550	-1.105474	0.550667
H	8.817611	0.971033	-0.701822
H	7.996050	1.695607	0.678704
H	9.744492	1.467171	0.723738
O	7.431549	-2.291677	0.242562
N	6.248517	-0.394597	0.586065
H	6.233282	0.609932	0.741458
C	4.943762	-0.882050	0.205461
H	5.029696	-1.441753	-0.730215
C	4.327739	-1.784690	1.268238
C	4.094048	0.380685	-0.035652
H	4.204848	-1.236973	2.204486
H	3.347678	-2.142286	0.951425
H	4.976674	-2.643654	1.440102
O	4.552659	1.487080	0.269703
N	2.901443	0.161360	-0.554850
H	2.488582	-0.765661	-0.753464
C	1.865743	1.147521	-0.778949
H	1.822040	1.806443	0.089331
C	2.164258	1.963563	-2.030370
C	0.561819	0.287700	-0.916900
H	2.156712	1.313127	-2.907381
H	1.415809	2.740566	-2.178296
H	3.145594	2.434328	-1.943031
O	0.773853	-0.926170	-1.111239
N	-0.625168	0.854838	-0.835566
C	-0.800407	2.238060	-0.427940
H	0.124852	2.716871	-0.095740
C	-1.340450	3.102542	-1.574221
C	-1.777026	2.302222	0.757120
H	-1.496305	4.115170	-1.189696
H	-0.573424	3.149124	-2.362920
O	-2.561123	2.669854	-2.120736
O	-1.803095	3.306755	1.484218
H	-2.587346	1.697785	-2.076168
N	-2.530574	1.213707	0.802717
C	-3.677784	1.049325	1.657677
H	-3.386339	0.832594	2.697756
C	-4.624122	2.260675	1.714152
C	-4.458575	-0.155388	1.132278
H	-4.066756	3.126957	2.064775
H	-4.973506	2.471380	0.692537
O	-5.707571	2.024642	2.591879
O	-5.595082	-0.423837	1.582473
H	-5.977102	1.103678	2.379531
N	-3.831939	-0.840956	0.178788
C	-4.559446	-1.892939	-0.508641
H	-5.408037	-1.470857	-1.057233
C	-3.600930	-2.579394	-1.487273
C	-5.146150	-2.966492	0.399351

H	-3.005053	-3.313856	-0.938224
H	-4.174646	-3.119018	-2.244167
S	-2.470139	-1.393932	-2.275362
O	-6.143852	-3.605444	0.108079
N	-4.388645	-3.262112	1.493798
H	-4.848121	-3.801413	2.207376
H	-3.749980	-2.541203	1.793595
H	10.096280	-1.028348	-0.254129
Ni	-2.278026	-0.078791	-0.524255

Table S5 Energies and Cartesian coordinates of the $NiH_{-3}L$ complex with (N^-,N^-,N^-,S^-) donors in water. L refers to AAASSC-NH_2.

Sum of electronic and zero-point Energies (Eh)	-3601.175651
Sum of electronic and thermal Energies (Eh)	-3601.138009
Sum of electronic and enthalpy Energies (Eh)	-3601.137065
Sum of electronic and thermal Free Energies (Eh)	-3601.247525
Number of Imaginary Frequencies	0

Molecular Geometry in Cartesian Coordinates

N	9.138890	-1.362902	1.628515
H	8.665337	-1.520782	2.512561
C	8.310376	-0.515526	0.782191
H	8.192064	0.448703	1.280784
C	8.987777	-0.299679	-0.559369
C	6.927144	-1.111473	0.549826
H	9.137413	-1.255040	-1.067780
H	8.390282	0.343541	-1.207129
H	9.961630	0.168730	-0.411324
O	6.788179	-2.288394	0.195654
N	5.893135	-0.285719	0.736288
H	6.062434	0.657804	1.055259
C	4.512855	-0.671442	0.530768
H	4.482232	-1.379975	-0.297541
C	3.904594	-1.319059	1.770683
C	3.730996	0.583105	0.170675
H	3.910478	-0.621828	2.609730
H	2.876644	-1.627067	1.575706
H	4.481533	-2.202530	2.045038
O	3.960801	1.650109	0.750775
N	2.789059	0.429459	-0.757480
H	2.695649	-0.464445	-1.219227
C	1.875290	1.483155	-1.178297
H	1.825285	2.188454	-0.355064
C	2.394161	2.192489	-2.419040
C	0.531810	0.776921	-1.453491
H	2.521525	1.484976	-3.238996
H	1.698485	2.969443	-2.740812
H	3.356909	2.660282	-2.207661
O	0.581326	-0.065788	-2.374001
N	-0.548047	1.010790	-0.714254
C	-0.549220	2.146745	0.215761
H	0.321627	2.141054	0.879085
C	-0.570147	3.494696	-0.506110
C	-1.770696	2.089398	1.113120

H	-0.631436	4.295686	0.231538
H	0.351747	3.632138	-1.077239
O	-1.696464	3.630872	-1.360729
O	-1.889168	2.895493	2.068271
H	-1.728018	2.837573	-1.912430
N	-2.631730	1.169412	0.746419
C	-3.906043	0.993061	1.393031
H	-3.802481	0.863246	2.478870
C	-4.860079	2.168737	1.155965
C	-4.518575	-0.266803	0.814253
H	-4.408681	3.087739	1.527422
H	-5.027402	2.281164	0.077168
O	-6.088734	1.978210	1.839001
O	-5.716954	-0.561563	1.066944
H	-6.315449	1.040422	1.663320
N	-3.705514	-0.958694	0.032263
C	-4.227732	-2.139449	-0.635227
H	-4.950229	-1.846016	-1.403721
C	-3.060839	-2.876719	-1.283281
C	-4.957278	-3.121845	0.268836
H	-2.568325	-3.498692	-0.532446
H	-3.425697	-3.540863	-2.068678
S	-1.835977	-1.715549	-1.972769
O	-5.938485	-3.750450	-0.144227
N	-4.416089	-3.348559	1.468364
H	-4.855909	-3.999346	2.099459
H	-3.660635	-2.772623	1.803325
H	9.217525	-2.274190	1.185599
Ni	-2.127401	-0.098966	-0.514878

Table S6 Energies and Cartesian coordinates of the $NiH_{-3}L$ complex with (NH_2,N^-,N^-,N^-) donors in gas phase. L refers to AAEAAC-NH_2.

Sum of electronic and zero-point Energies (Eh)	-3677.964158
Sum of electronic and thermal Energies (Eh)	-3677.924891
Sum of electronic and enthalpy Energies (Eh)	-3677.923946
Sum of electronic and thermal Free Energies (Eh)	-3678.04298
Number of Imaginary Frequencies	0

Molecular Geometry in Cartesian Coordinates

N	-1.407269	-2.354496	1.447808
H	-1.860790	-2.340685	2.356139
C	-1.572795	-3.683597	0.826461
H	-0.703858	-3.833029	0.177997
C	-1.631906	-4.813997	1.834934
C	-2.787896	-3.688250	-0.118823
H	-2.449138	-4.650843	2.545068
H	-1.833154	-5.747435	1.308487
H	-0.697768	-4.902244	2.395740
O	-3.179497	-4.761471	-0.607890
N	-3.235003	-2.466039	-0.333776
C	-4.226920	-2.152525	-1.337952
H	-4.000764	-2.695205	-2.264408
C	-5.644441	-2.511587	-0.910344
C	-4.131625	-0.647019	-1.643310

H	-5.889831	-2.002378	0.024906
H	-6.348863	-2.183169	-1.677168
H	-5.731915	-3.589680	-0.763140
O	-4.788863	-0.154054	-2.567267
N	-3.304046	-0.019372	-0.808656
C	-3.027369	1.403007	-0.859190
H	-2.886187	1.726458	-1.896150
C	-4.171007	2.232311	-0.232336
C	-1.712845	1.600329	-0.107738
H	-5.096295	1.840726	-0.663080
H	-4.218917	2.027982	0.839740
C	-4.109115	3.734891	-0.456714
O	-0.989970	2.589324	-0.284647
H	-3.150107	4.124829	-0.099179
H	-4.146174	3.965708	-1.525722
C	-5.227001	4.559927	0.247284
O	-5.720212	4.077791	1.291858
O	-5.503111	5.657487	-0.293789
N	-1.454480	0.604499	0.776049
C	-0.330143	0.840600	1.663729
H	-0.105013	1.910760	1.611169
C	-0.641566	0.484611	3.106272
C	0.891913	0.095209	1.141642
H	-0.820682	-0.582172	3.236423
H	0.190241	0.759573	3.760693
H	-1.534009	1.027428	3.419223
O	1.171497	-1.060762	1.476421
N	1.615268	0.792136	0.245523
H	1.236113	1.690386	-0.033531
C	2.666524	0.199210	-0.542200
H	2.722726	-0.842953	-0.223119
C	2.329119	0.273237	-2.029950
C	4.024200	0.878401	-0.308251
H	2.244352	1.315416	-2.343533
H	3.108041	-0.204726	-2.627272
H	1.377023	-0.222494	-2.222062
O	4.123674	2.084431	-0.159242
N	5.070871	0.028315	-0.353008
H	4.913521	-0.931869	-0.631346
C	6.457937	0.429320	-0.452849
H	6.517318	1.398442	-0.955559
C	7.133811	0.593844	0.931120
C	7.153041	-0.635115	-1.301177
H	6.472371	1.253266	1.495764
H	7.116551	-0.383083	1.428859
S	8.817548	1.291107	0.916385
O	6.565088	-1.646997	-1.683916
N	8.443938	-0.370638	-1.568190
H	8.963200	-1.163549	-1.916768
H	8.901579	0.274556	-0.862513
H	-0.422827	-2.096241	1.583313
Ni	-2.326171	-1.019470	0.355098

Table S7 Energies and Cartesian coordinates of the $NiH_{-3}L$ complex with (NH_2,N^-,N^-,N^-) donors in water. L refers to AAEAAC-NH_2.

Sum of electronic and zero-point Energies (Eh)	-3678.42819
Sum of electronic and thermal Energies (Eh)	-3678.389

Sum of electronic and enthalpy Energies (Eh)	-3678.388056
Sum of electronic and thermal Free Energies (Eh)	-3678.506475
Number of Imaginary Frequencies	0

Molecular Geometry in Cartesian Coordinates

N	-1.961848	-2.528224	1.374976
H	-2.549579	-2.490684	2.204984
C	-2.271739	-3.760717	0.612752
H	-1.332164	-4.113403	0.178324
C	-2.853658	-4.849360	1.490996
C	-3.171138	-3.419326	-0.568578
H	-3.784288	-4.511586	1.954489
H	-3.067480	-5.740747	0.901230
H	-2.152261	-5.122110	2.280950
O	-3.600158	-4.327320	-1.318092
N	-3.372831	-2.124293	-0.702967
C	-4.064710	-1.548768	-1.842026
H	-3.697354	-2.003520	-2.770158
C	-5.577142	-1.720495	-1.789203
C	-3.702930	-0.067227	-1.880865
H	-5.988124	-1.261089	-0.887579
H	-6.039186	-1.248011	-2.657446
H	-5.844750	-2.777127	-1.791971
O	-4.097482	0.668093	-2.816115
N	-2.969455	0.311271	-0.848711
C	-2.515301	1.666396	-0.647627
H	-2.084759	2.071303	-1.571261
C	-3.663447	2.587027	-0.197350
C	-1.408409	1.608821	0.395583
H	-4.515415	2.371226	-0.845358
H	-3.960554	2.305831	0.816652
C	-3.354219	4.069999	-0.267432
O	-0.682493	2.612420	0.580527
H	-2.530365	4.327611	0.402362
H	-3.011343	4.338668	-1.271269
C	-4.509670	5.000866	0.083804
O	-5.574093	4.513306	0.543898
O	-4.309796	6.233342	-0.103277
N	-1.330271	0.448872	1.057598
C	-0.312160	0.364043	2.102087
H	0.150212	1.348910	2.194807
C	-0.883807	-0.019142	3.452434
C	0.780803	-0.600413	1.653747
H	-1.375694	-0.990926	3.437789
H	-0.093071	-0.052064	4.204559
H	-1.615348	0.727947	3.762811
O	0.794286	-1.796912	1.975922
N	1.720454	-0.065335	0.870175
H	1.661547	0.912776	0.618768
C	2.765279	-0.838634	0.237832
H	3.104888	-1.594936	0.946226
C	2.284042	-1.523411	-1.039409
C	3.917411	0.100657	-0.084424
H	1.992367	-0.782111	-1.785037
H	3.072087	-2.150378	-1.457755
H	1.423640	-2.154837	-0.817119
O	3.717729	1.299206	-0.305323
N	5.119114	-0.470330	-0.144068

H	5.200809	-1.474369	-0.043195
C	6.311321	0.223787	-0.578295
H	6.057517	0.866680	-1.426334
C	6.899792	1.120348	0.527605
C	7.299828	-0.831828	-1.057955
H	6.054486	1.629289	0.993014
H	7.343519	0.475938	1.293710
S	8.101126	2.356515	-0.064736
O	7.004433	-2.034392	-1.065965
N	8.473143	-0.353950	-1.460657
H	9.207725	-1.010391	-1.681985
H	8.683610	0.632239	-1.210328
H	-0.993277	-2.528118	1.701528
Ni	-2.375851	-0.962501	0.313618

Table S8 Energies and Cartesian coordinates of the $NiH_{-3}L$ complex with (N^-,N^-,N^-,S^-) donors in gas phase. L refers to AAEAAC-NH_2.

Sum of electronic and zero-point Energies (Eh)	-3677.924573
Sum of electronic and thermal Energies (Eh)	-3677.884793
Sum of electronic and enthalpy Energies (Eh)	-3677.883849
Sum of electronic and thermal Free Energies (Eh)	-3678.004491
Number of Imaginary Frequencies	0

Molecular Geometry in Cartesian Coordinates

N	8.515076	-3.332561	0.715022
H	8.134274	-3.997350	0.041708
C	7.365067	-2.592721	1.222985
H	6.980777	-3.132239	2.098772
C	7.787705	-1.203100	1.667115
C	6.209155	-2.597353	0.197099
H	8.100173	-0.602188	0.808952
H	6.987052	-0.660450	2.168752
H	8.628770	-1.279717	2.359935
O	6.265279	-3.347474	-0.776540
N	5.184396	-1.799002	0.479015
H	5.192102	-1.126416	1.247452
C	4.001534	-1.596642	-0.326963
H	4.296011	-1.455783	-1.369891
C	3.020412	-2.758290	-0.227998
C	3.381437	-0.286615	0.214871
H	2.707240	-2.897201	0.808668
H	2.127786	-2.562218	-0.823647
H	3.492767	-3.675058	-0.583794
O	3.810553	0.171762	1.279330
N	2.422268	0.212023	-0.538220
H	1.965661	-0.344337	-1.278593
C	1.487565	1.277605	-0.200842
H	1.530341	1.425380	0.878311
C	1.853188	2.581131	-0.925464
C	0.108953	0.682705	-0.673836
H	1.758271	2.409117	-2.002370
H	1.117866	3.348135	-0.682243
C	3.241711	3.114542	-0.603987
O	0.218631	-0.202648	-1.549967

H	3.339481	3.247078	0.480808
H	4.012853	2.391556	-0.880485
C	3.619699	4.478885	-1.254022
O	2.679943	5.230407	-1.591304
O	4.851809	4.697927	-1.343135
N	-1.037135	1.097507	-0.164487
C	-1.085514	2.058165	0.926696
H	-0.118921	2.187059	1.418406
C	-1.570563	3.430422	0.452338
C	-2.076163	1.573781	1.990766
H	-2.533668	3.314880	-0.050432
H	-1.690222	4.099563	1.307879
H	-0.866235	3.875201	-0.251830
O	-2.060532	2.039953	3.144917
N	-2.936243	0.710438	1.472983
C	-4.142974	0.301554	2.136389
H	-3.927143	-0.353819	2.997132
C	-4.985735	1.469390	2.646016
C	-4.960576	-0.529115	1.149854
H	-5.234332	2.132280	1.812705
H	-5.914787	1.090317	3.075600
H	-4.414753	2.033781	3.381907
O	-6.143482	-0.834219	1.470663
N	-4.324040	-0.834817	0.029807
C	-4.999849	-1.544593	-1.063461
H	-5.912219	-0.984873	-1.320273
C	-4.070164	-1.597118	-2.266875
C	-5.463350	-2.986460	-0.723032
H	-3.407140	-2.453371	-2.142562
H	-4.657649	-1.785748	-3.171856
S	-3.083629	-0.090048	-2.465071
O	-4.995767	-3.988012	-1.251512
N	-6.487796	-3.053816	0.160473
H	-6.662645	-3.978934	0.521455
H	-6.573198	-2.213622	0.776167
H	9.064336	-2.694202	0.146151
Ni	-2.745756	0.188819	-0.303548

Table S9 Energies and Cartesian coordinates of the $NiH_{-3}L$ complex with (N^-,N^-,N^-,S^-) donors in water. L refers to AAEAAC-NH_2.

Sum of electronic and zero-point Energies (Eh)	-3678.427905
Sum of electronic and thermal Energies (Eh)	-3678.388171
Sum of electronic and enthalpy Energies (Eh)	-3678.387227
Sum of electronic and thermal Free Energies (Eh)	-3678.505071
Number of Imaginary Frequencies	0

Molecular Geometry in Cartesian Coordinates

N	8.620941	-3.057032	0.608399
H	8.076656	-3.797567	1.039892
C	7.823251	-1.839761	0.558973
H	7.590991	-1.546376	1.584455
C	8.610147	-0.726249	-0.109991
C	6.513698	-2.037338	-0.193861
H	8.867809	-1.006060	-1.134140

H	8.035472	0.200620	-0.141534
H	9.533667	-0.542065	0.440442
O	6.487905	-2.601894	-1.294686
N	5.418429	-1.552587	0.395947
H	5.490570	-1.099267	1.296638
C	4.099875	-1.604442	-0.194584
H	4.205195	-1.491802	-1.274450
C	3.386129	-2.919011	0.106808
C	3.297858	-0.434489	0.359905
H	3.230203	-3.033812	1.180841
H	2.418411	-2.953566	-0.394478
H	3.989162	-3.753852	-0.251105
O	3.540540	0.014880	1.485774
N	2.328852	0.017464	-0.432253
H	2.186722	-0.415371	-1.334818
C	1.375464	1.052178	-0.070575
H	1.450430	1.182069	1.004898
C	1.701404	2.381097	-0.760160
C	-0.015962	0.583355	-0.525213
H	1.726659	2.214742	-1.839538
H	0.878382	3.074191	-0.569613
C	3.006629	2.989513	-0.287434
O	-0.061279	0.174782	-1.711916
H	2.973252	3.169931	0.791583
H	3.835942	2.293315	-0.444114
C	3.404000	4.306627	-0.947335
O	2.654445	4.802626	-1.826447
O	4.485894	4.822004	-0.552003
N	-1.061737	0.647785	0.280326
C	-0.874644	0.947125	1.703493
H	0.043782	0.491191	2.082028
C	-0.843780	2.441153	2.013714
C	-2.008433	0.322889	2.498793
H	-1.752450	2.923705	1.646260
H	-0.775624	2.604282	3.090961
H	0.012433	2.925707	1.543739
O	-1.907000	0.191097	3.746185
N	-3.038537	0.005332	1.750139
C	-4.290157	-0.490577	2.276714
H	-4.135937	-1.422909	2.834514
C	-5.015755	0.503105	3.179713
C	-5.172063	-0.811723	1.083279
H	-5.198877	1.437587	2.644230
H	-5.975517	0.091053	3.494760
H	-4.427351	0.722827	4.069208
O	-6.288385	-1.371035	1.254000
N	-4.661475	-0.446621	-0.080246
C	-5.432547	-0.586294	-1.310105
H	-6.493153	-0.395345	-1.090789
C	-4.916452	0.447819	-2.284125
C	-5.427729	-2.001714	-1.900796
H	-5.272015	0.241222	-3.293304
H	-5.302688	1.425266	-1.988670
S	-3.088315	0.469611	-2.265499
O	-5.363346	-2.213475	-3.115051
N	-5.563885	-2.992216	-1.013194
H	-5.680204	-3.934426	-1.353152
H	-5.810421	-2.766852	-0.054898
H	8.797107	-3.359790	-0.345611
Ni	-2.897124	0.177187	-0.093579

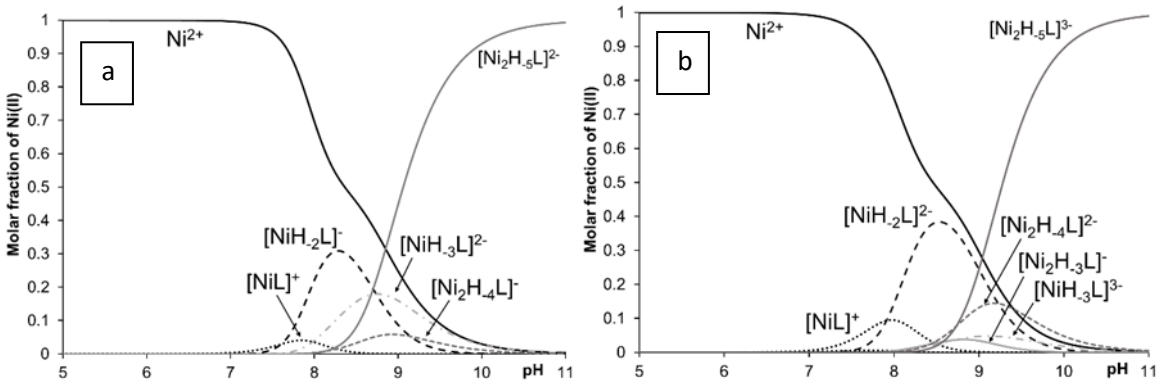
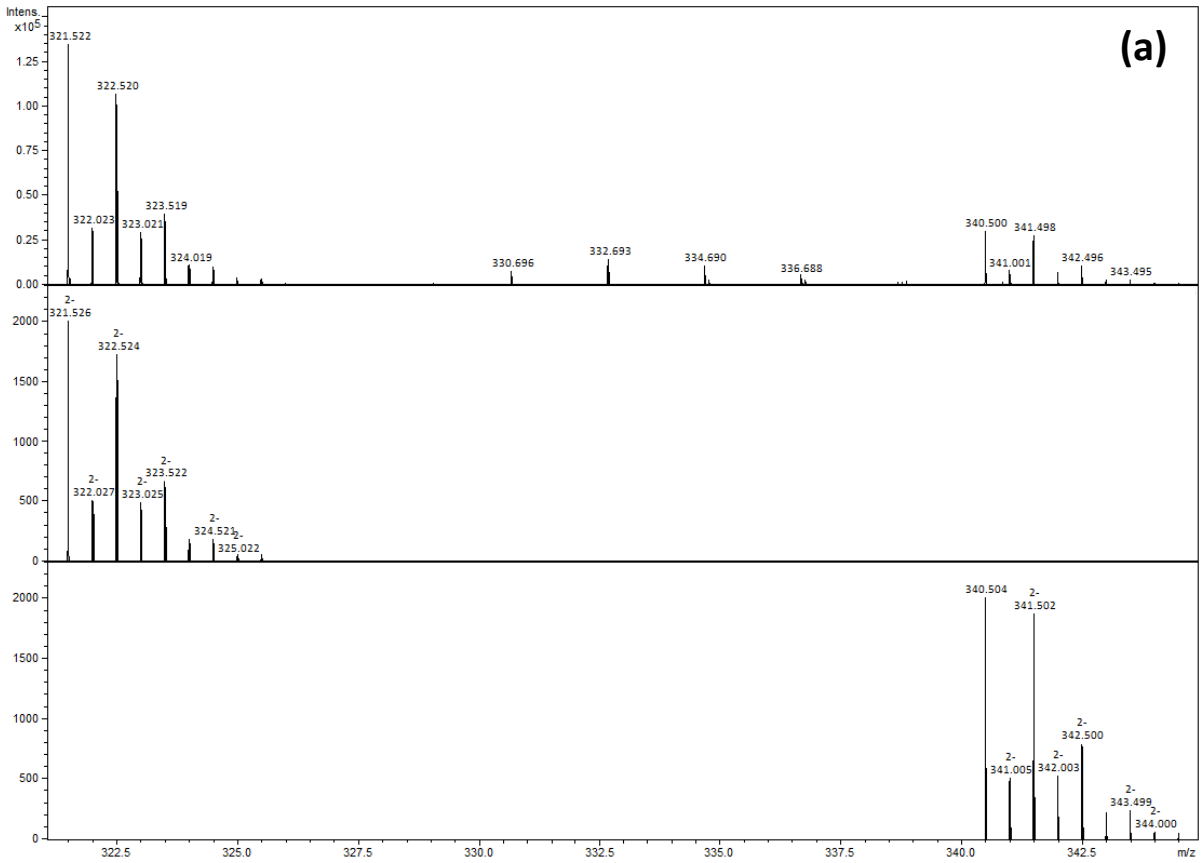


Figure S7 Distribution curves of the nickel(II) – ligand = 2:1 system of AAASSC-NH_2 (a) and AAEAAC-NH_2 (b) (c_L = 10 μM, $c_{Ni^{2+}}$ = 20 μM)



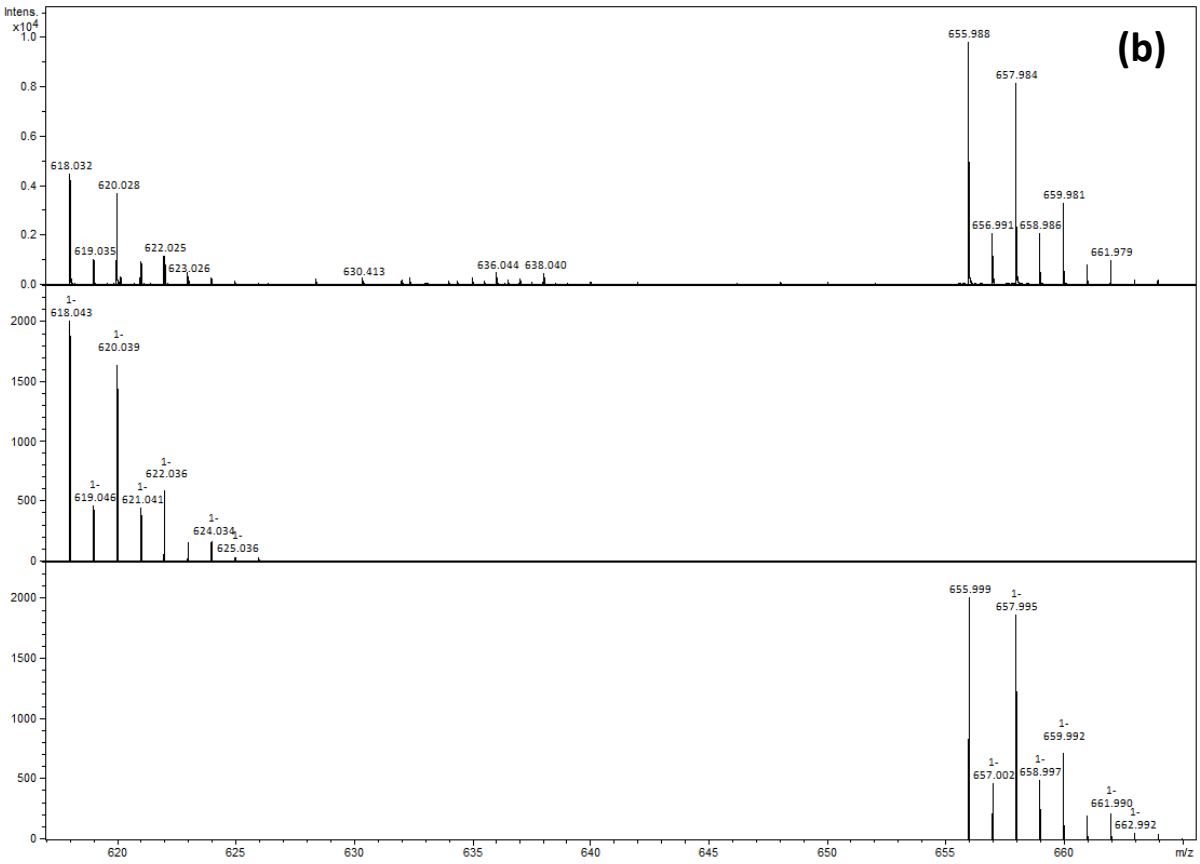


Figure S8 ESI-MS spectra of the $Ni_2H_{-5}L$ complexes of AAEAAC-NH_2 (a) and AAASSC-NH_2 (b) Spectra from up to bottom: measured spectrum, calculated spectra of $[M+H^+]$ and $[M+K^+]$ adducts

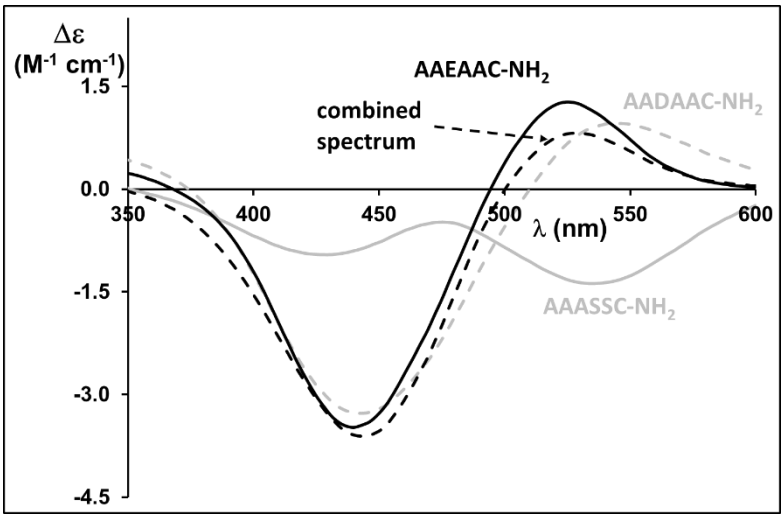


Figure S9 CD-spectra of the nickel(II) : ligand = 2:1 systems of AAEAAC-NH_2, AADAAC-$NH_2$and AAASSC-NH_2 and a calculated spectrum assuming 50-50% of Ac-DAAC-NH_2 and AAAC-NH_2 representing the equal occupation of the N-terminal and C-terminal binding domains

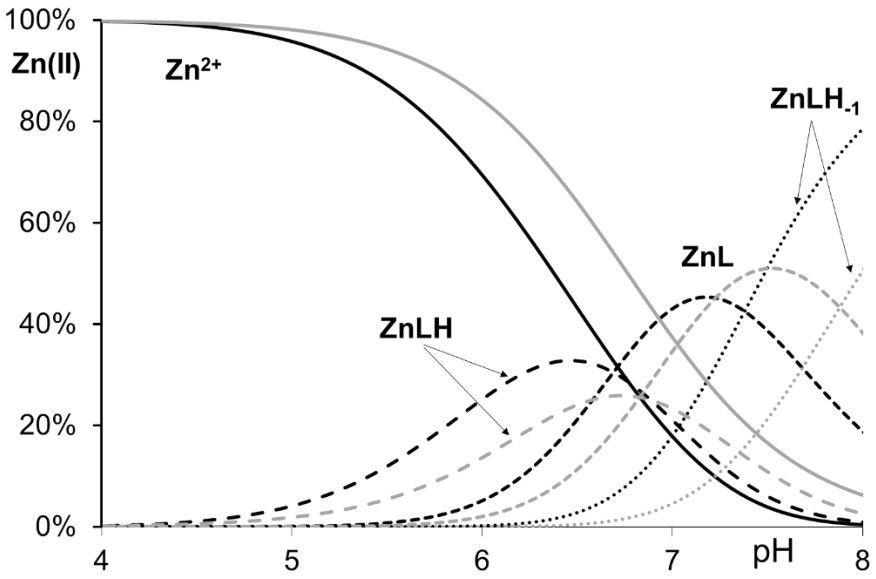


Figure S10 Complex distribution curves of the Zn(II) – ligand equimolar systems (AAASSC-NH_2 – grey lines, AAEAAC-NH_2 – black lines; c_L = 2.0 mM, $c_{Zn^{2+}}$ = 1.8 mM)

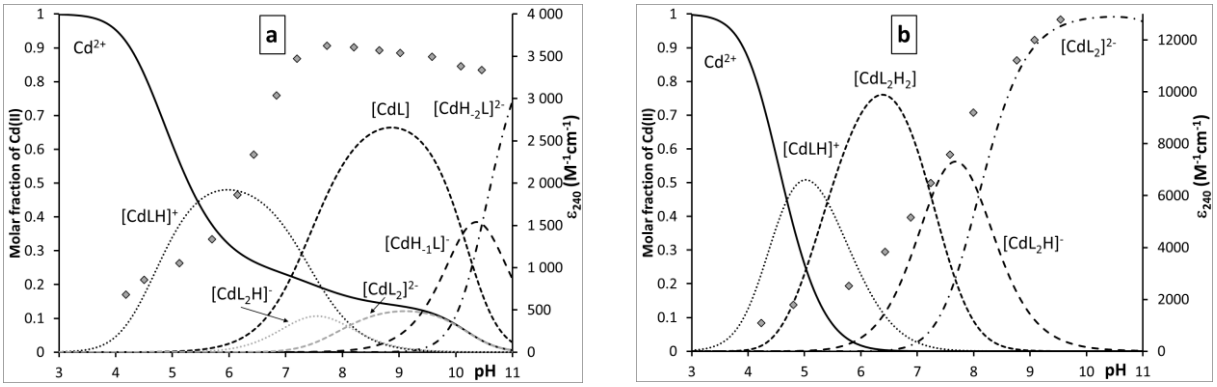


Figure S11 Complex distribution curves of the Cd(II) – AAEAAC-NH_2 equimolar (a) and ligand excess containing systems (b) (c_L = 2.0 mM, $c_{Zn^{2+}}$ = 1.8 mM or 0.70 mM)

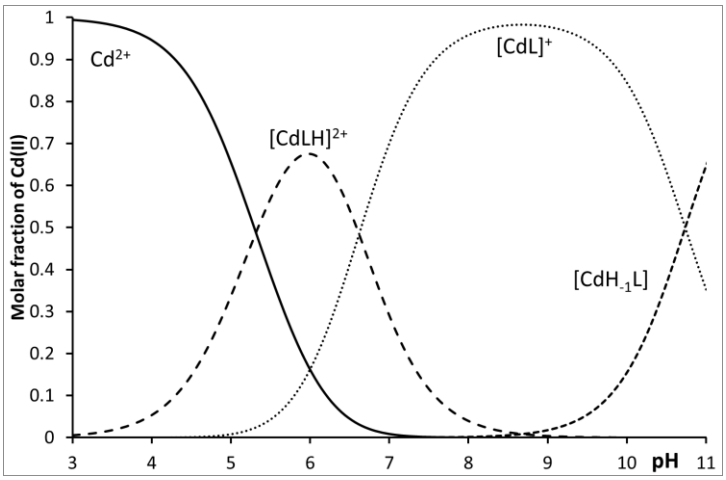


Figure S12 Complex distribution curves of the Cd(II) – AAASSC-NH_2 equimolar system (c_L = 2.0 mM, $c_{Zn^{2+}}$ = 1.8 mM)

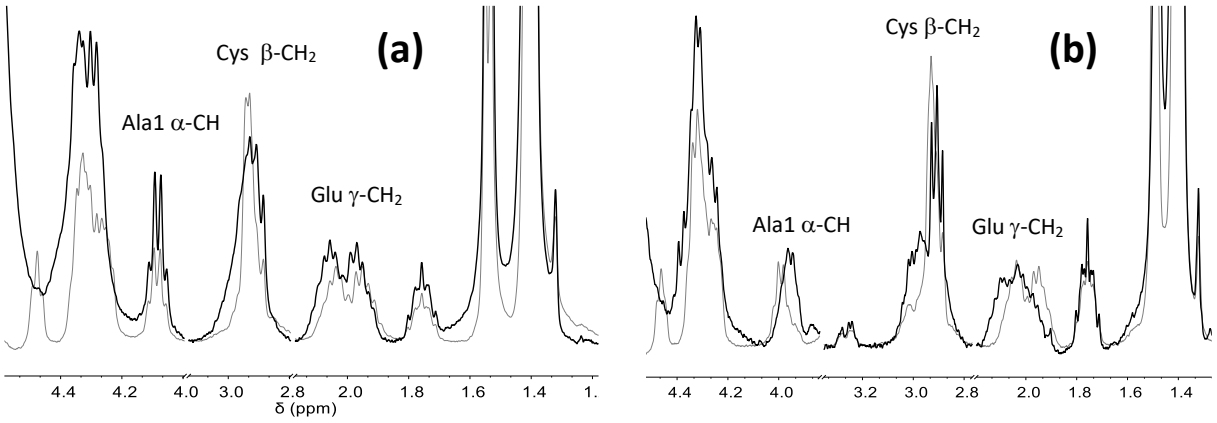


Figure S13: ^{1}H NMR spectra of the free ligand AAEAAC-NH_2 (black) and the zinc(II) containing system (grey) at pD=6.4 (a) and pD=7.8 (b) (c_L = 5.0 mM, $c_{Zn^{2+}}$ = 2.5mM)