Electronic Supplementary Material (ESI) for Metallomics

Supplementary materials

Unexpected impact of the number of glutamine residues on metal complex stability

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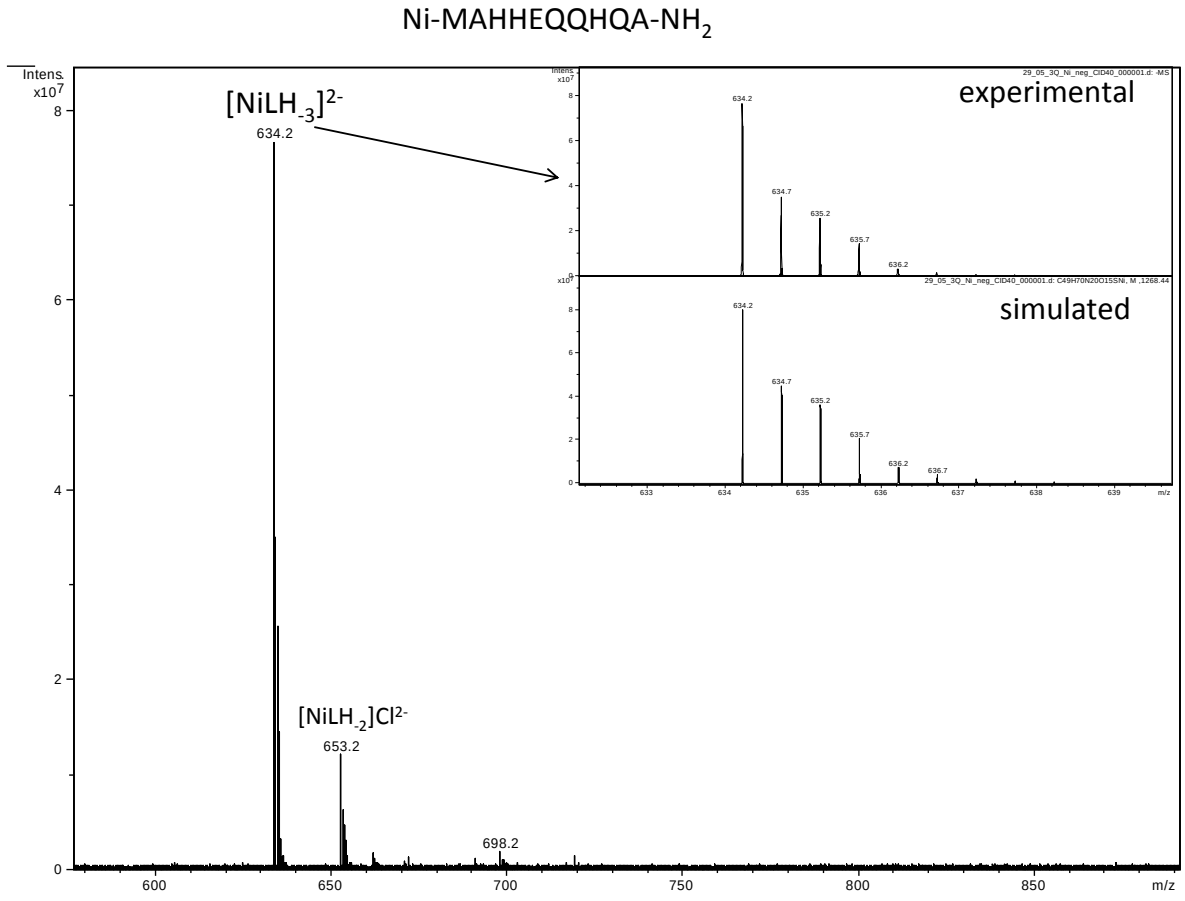
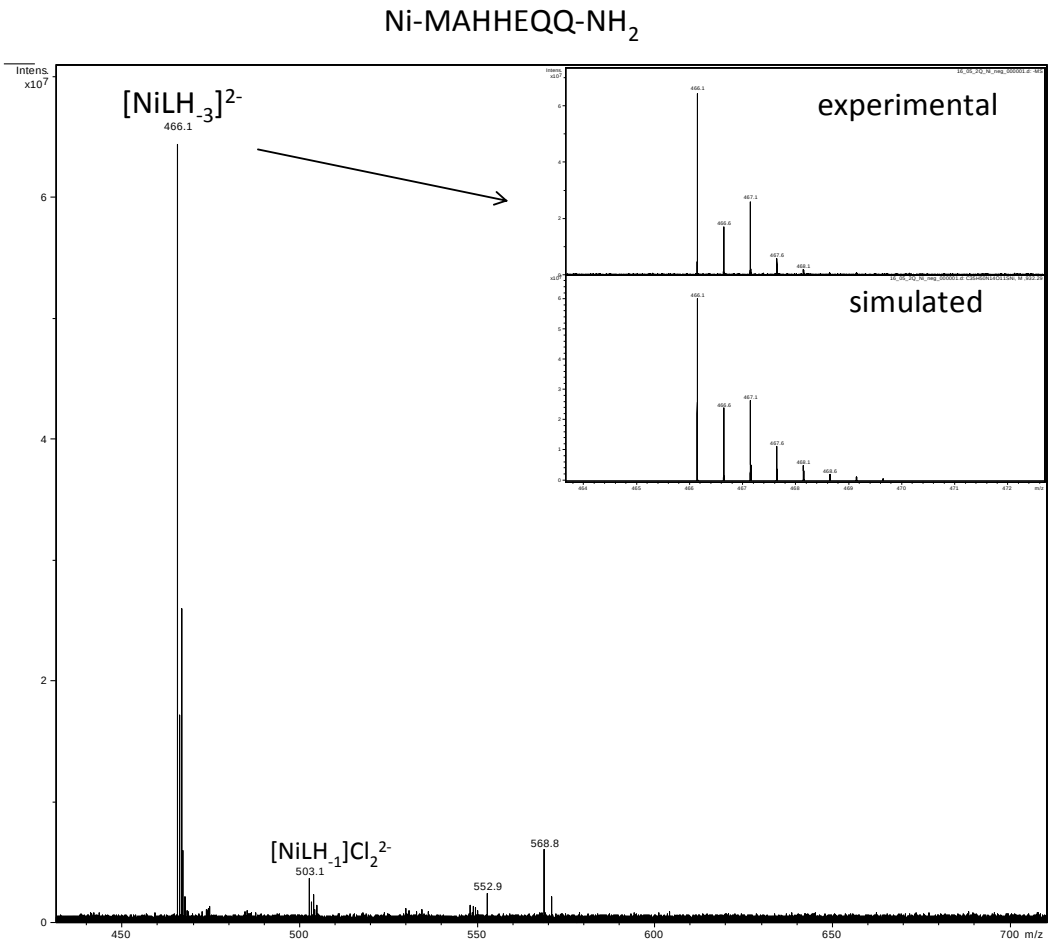
FIGURE S1 ESI-MS spectra of the studied systems. Metal : ligand ratio = 1:1.1, $[ligand]_{tot}$= 10^{-4} M), pH 7.4.

The most intensive signal on each of the plots corresponds to the metal complex, described in the text. The signal is enlarged in the upper right corner and its isotopic distribution is compared to a simulated one. Minor species on the main plot are Na and Cl adducts, and on plot H, also a minor signal from the free ligand is present. All species are negatively charged.

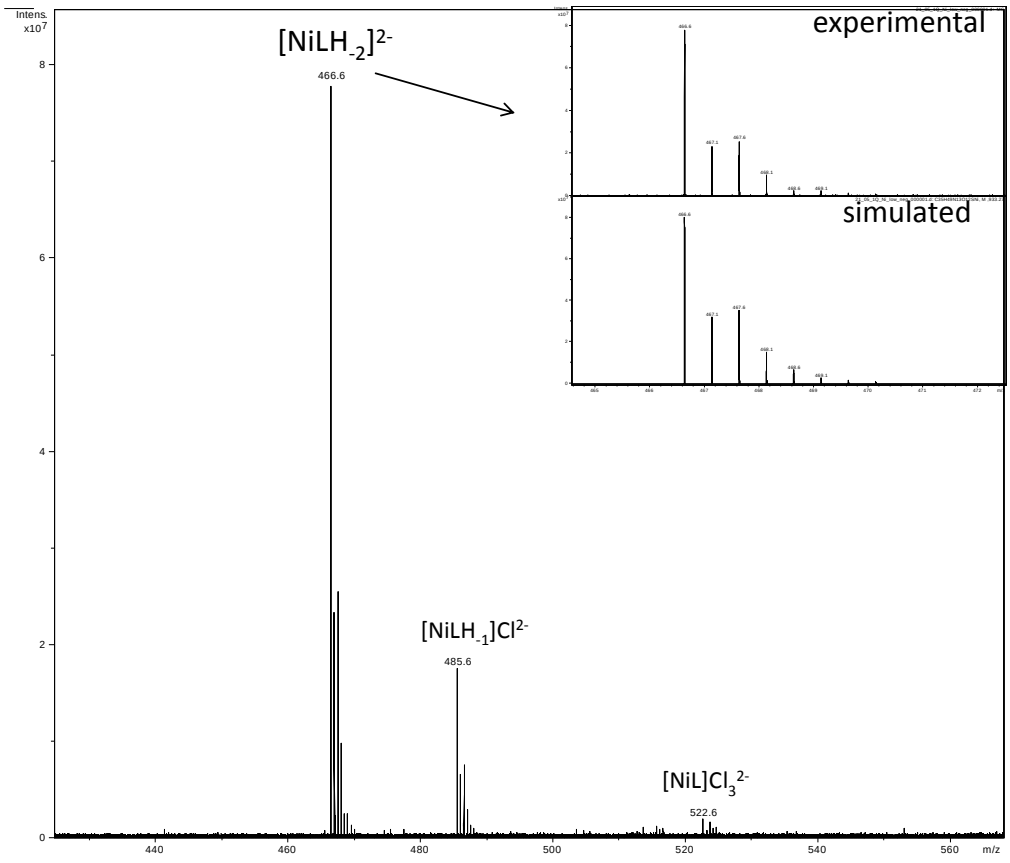
A Mass spectrum Ni^{2+} – MAHHEQQHQA-NH_2



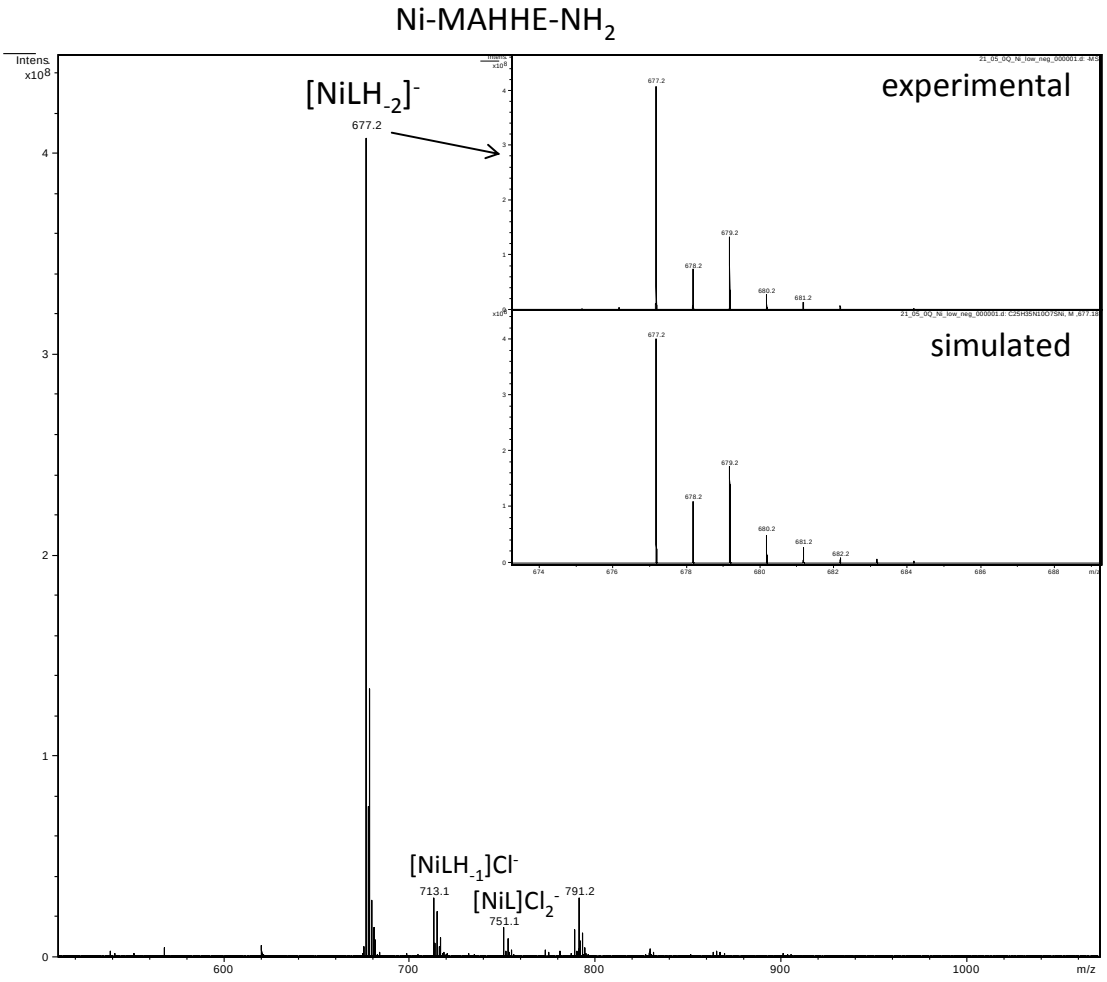
B Mass spectrum Ni^{2+} – MAHHEQQ-NH_2



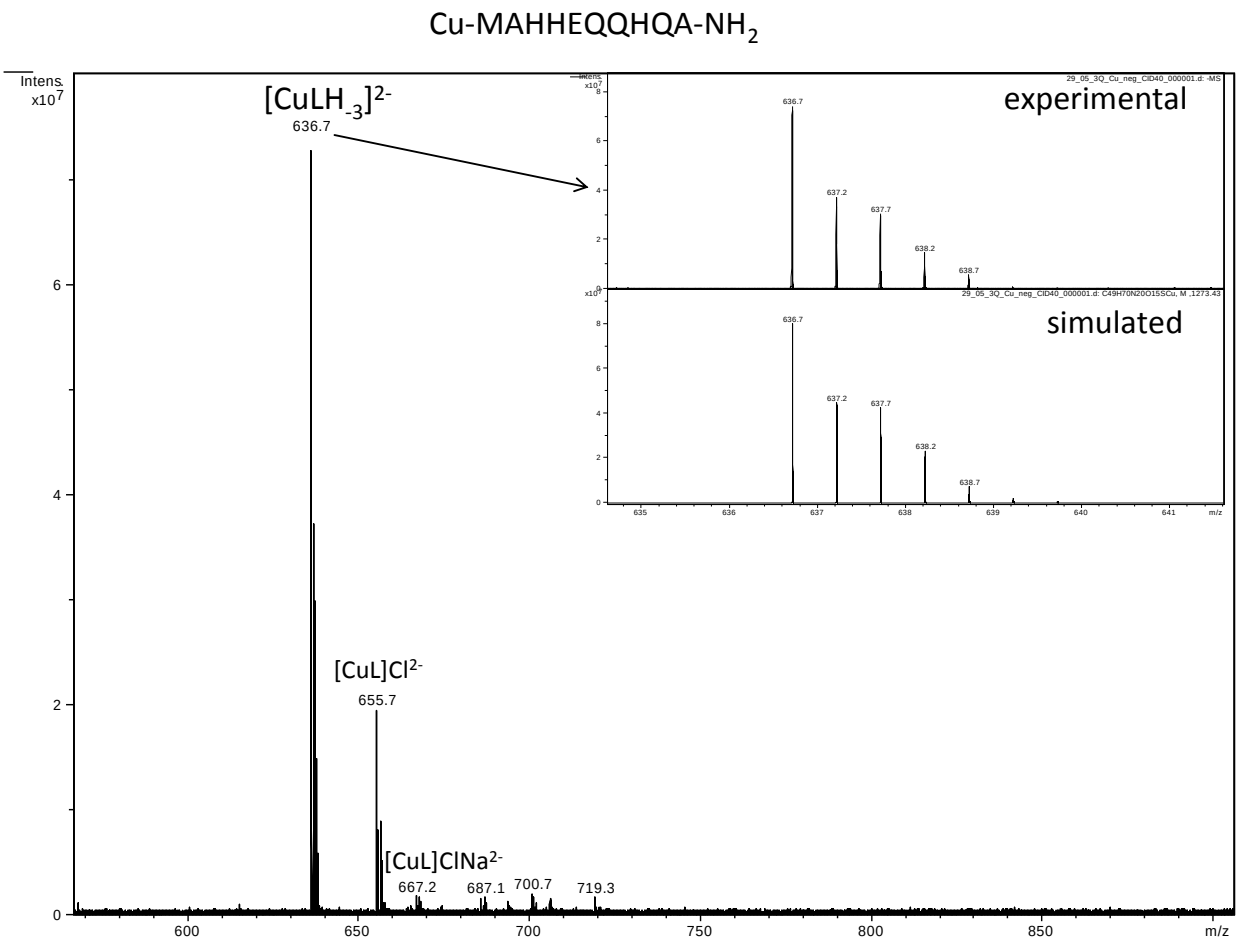
C Mass spectrum Ni^{2+} – MAHHEEQ-NH_2



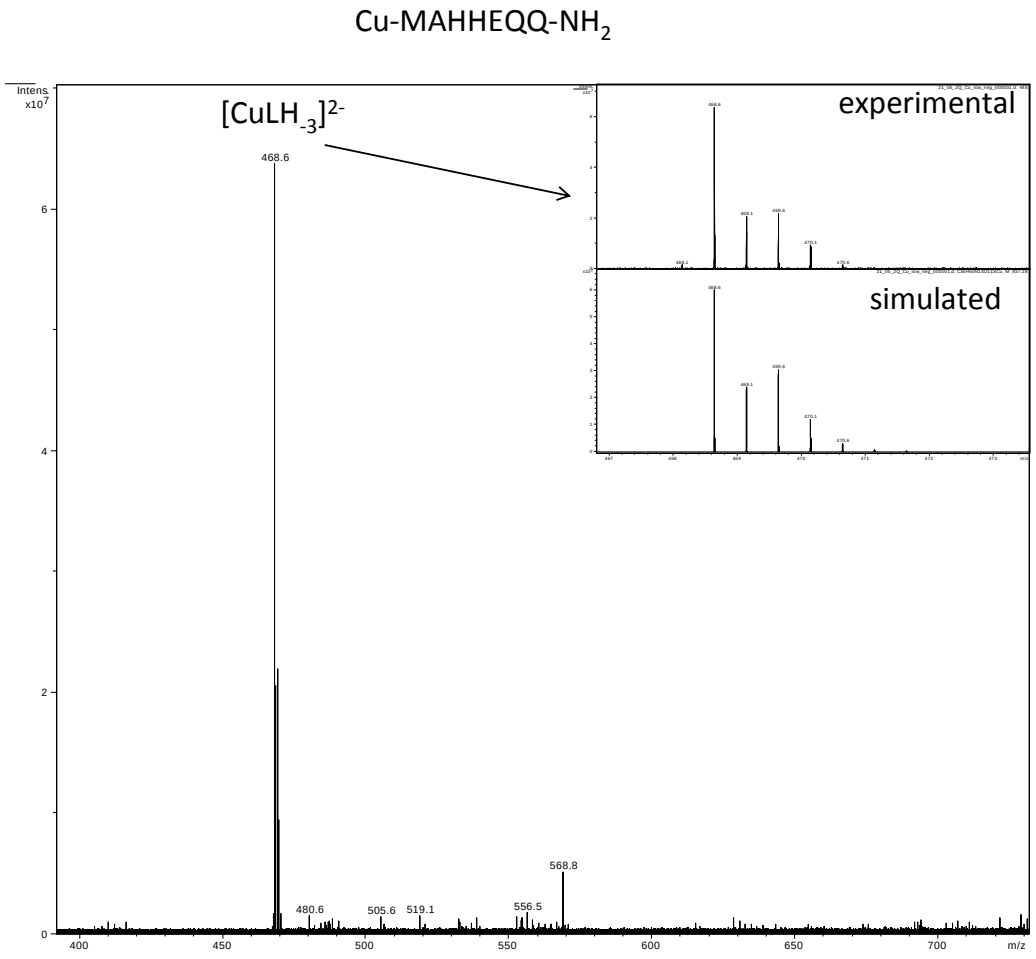
D Mass spectrum Ni^{2+} – MAHHE-NH_2



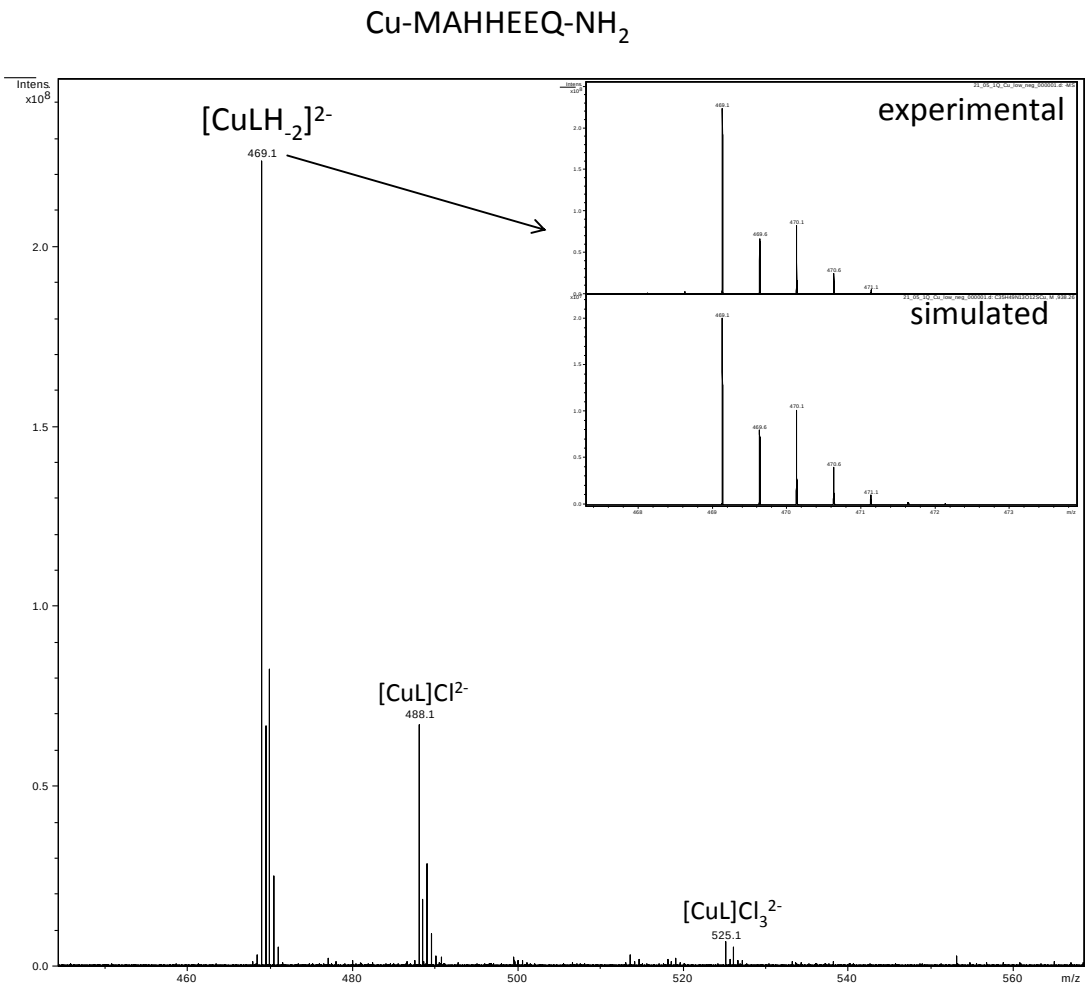
E Mass spectrum Cu^{2+} – MAHHEQQHQA-NH_2



F Mass spectrum Cu^{2+} – MAHHEQQ-NH_2



G Mass spectrum Cu^{2+} – MAHHEEQ-NH_2



H Mass spectrum Cu^{2+} – MAHHE-NH_2

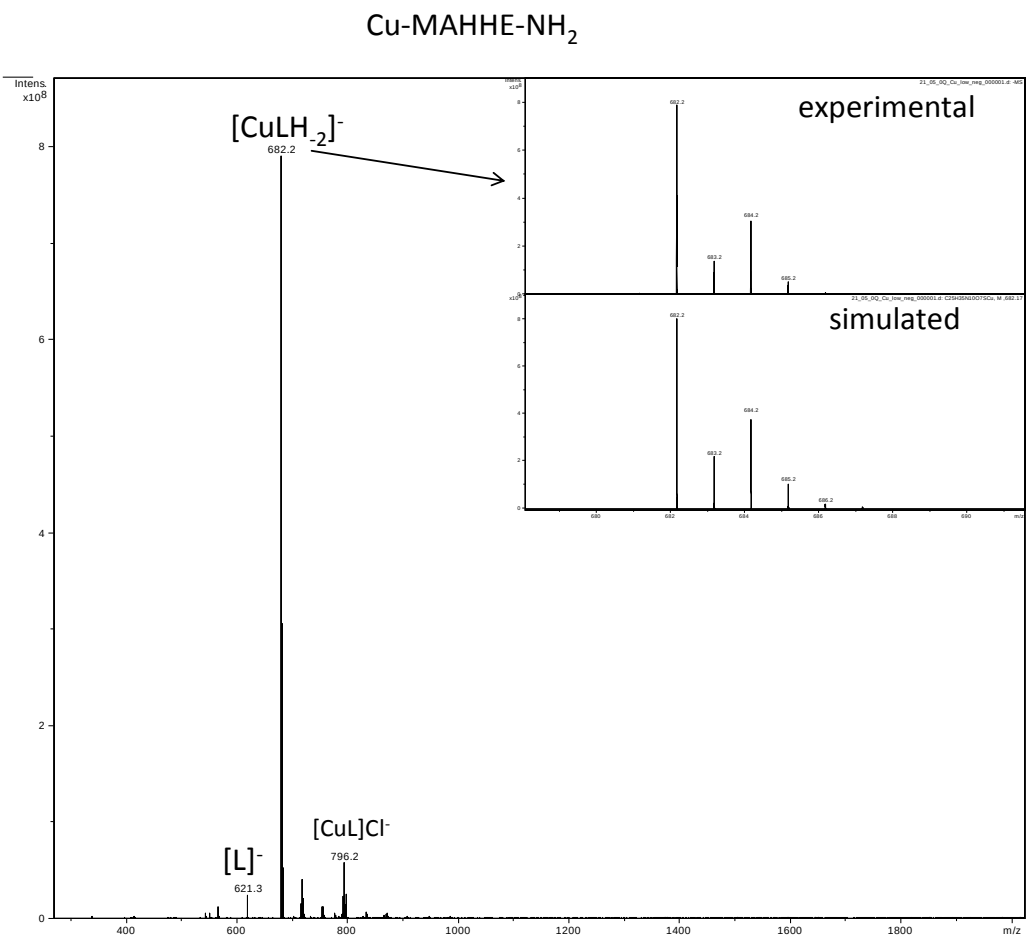
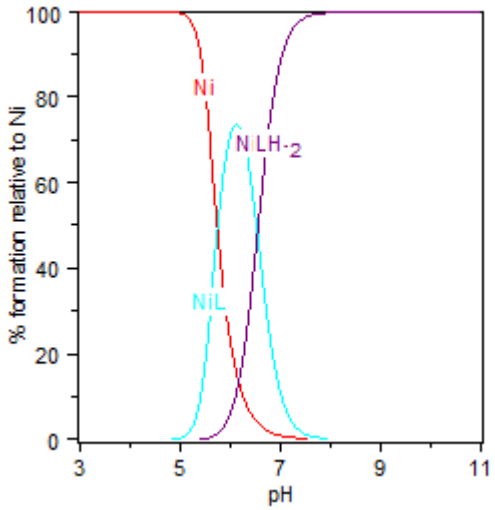
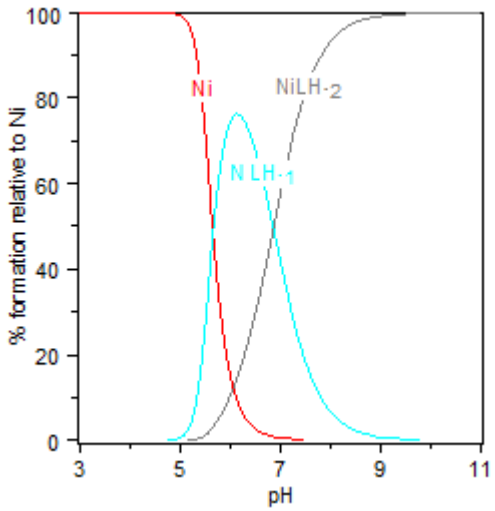


FIGURE S2. Distribution plots of the studied systems. Metal : ligand ratio = 1:1, $[ligand]_{tot}= 10^{-3}$ M), I=0,1M, 298K. All plots are based on a series of potentiometric titrations. A correlation between the species distribution and spectral parameters can be found in the tables; a wider description of this correlation is discussed in the main body of this paper.

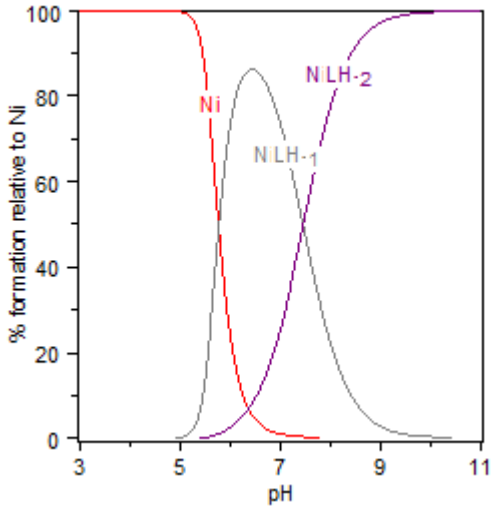
A Distribution plot Ni^{2+} – MAHHEQQHQA-NH_2



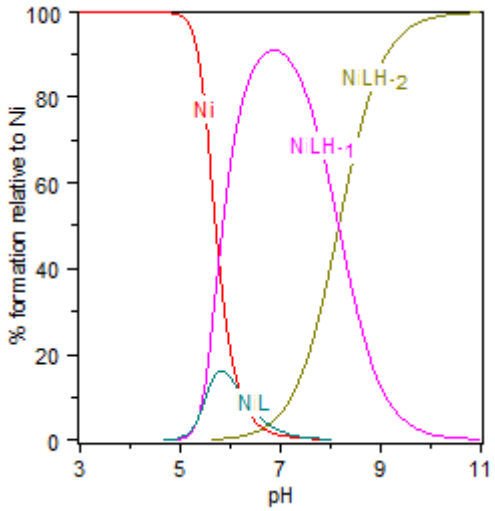
B Distribution plot Ni^{2+} – MAHHEQQ-NH_2



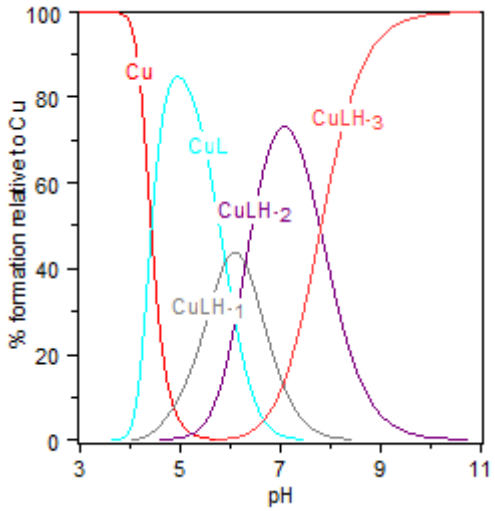
C Distribution plot Ni^{2+} – MAHHEEQ-NH_2



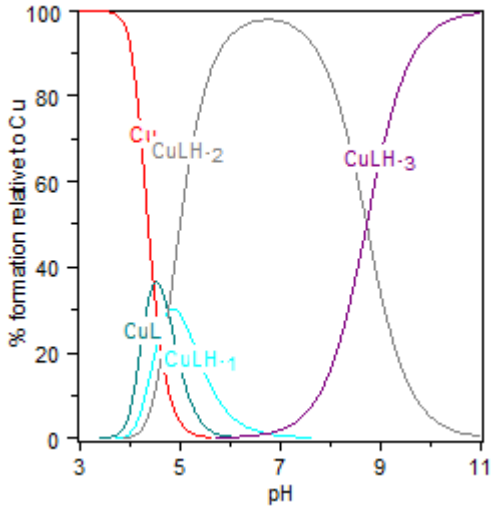
D Distribution plot Ni^{2+} – MAHHE-NH_2



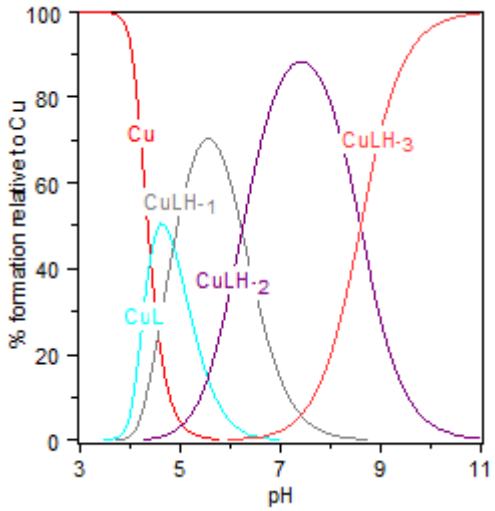
E Distribution plot Cu^{2+} – MAHHEQQHQA-NH_2



F Distribution plot Cu^{2+} – MAHHEQQ-NH_2



G Distribution plot Cu^{2+} – MAHHEEQ-NH_2



H Distribution plot Cu^{2+} – MAHHE-NH_2

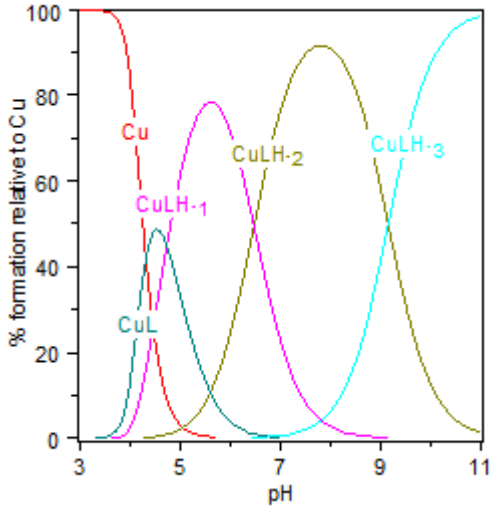
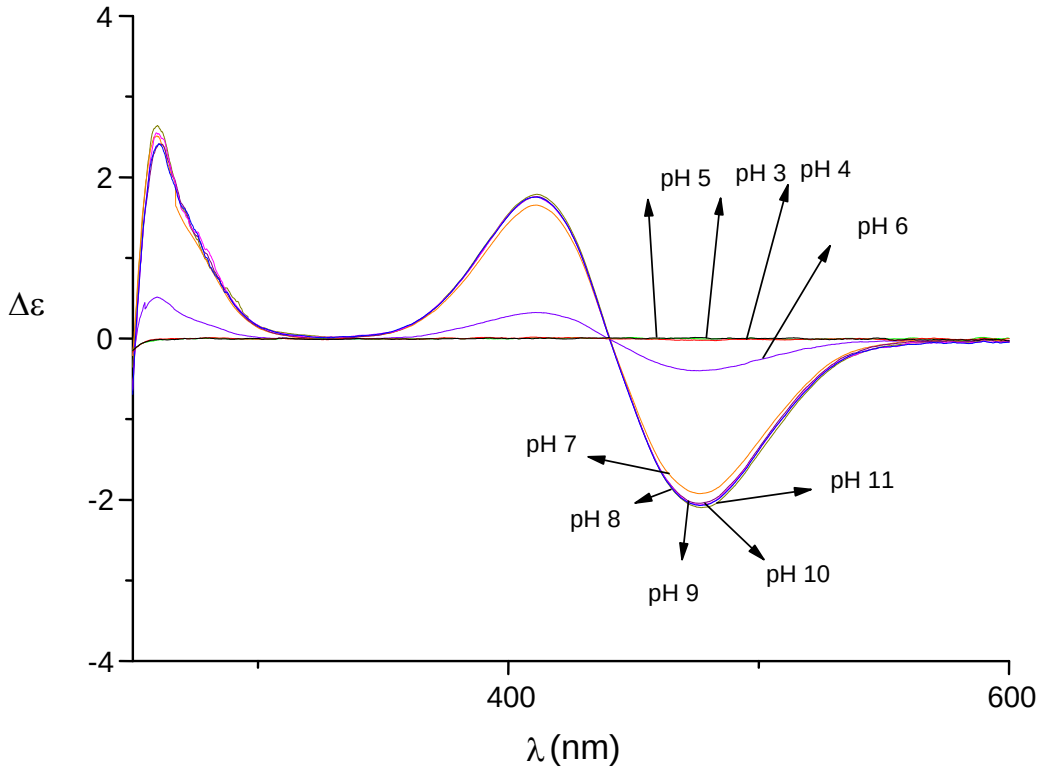
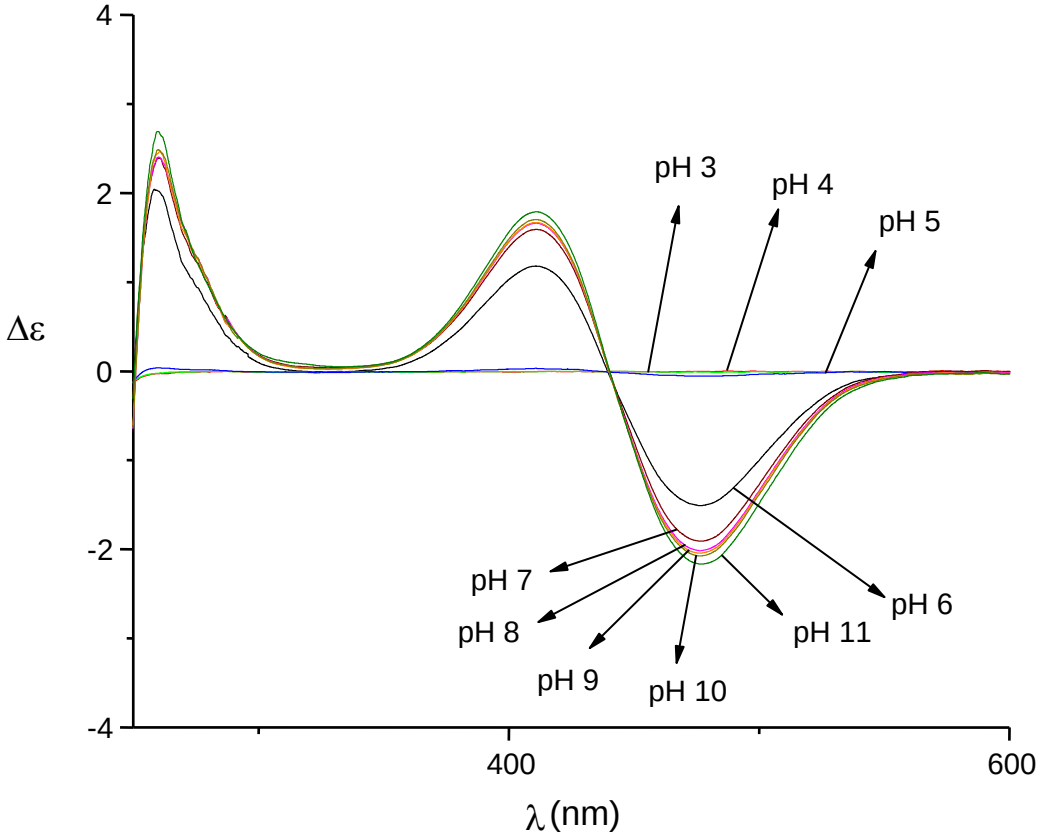


FIGURE S3. Circular dichroism spectra of the studied systems. Metal : ligand ratio = 1:1.1, $[ligand]_{tot}= 10^{-3}$ M), I=0,1M, (4mM HCl and 0.096M KCl), 298K. The studied pH ranges from 2 to 11. On all plots, the change of the spectral shape and intensity between pH 6 and 7 (together with potentiometric data) strongly suggests a square planar, albumine-like binding mode. A correlation between the species distribution and spectral parameters can be found in the tables; a wider description of this correlation is discussed in the main body of this paper.

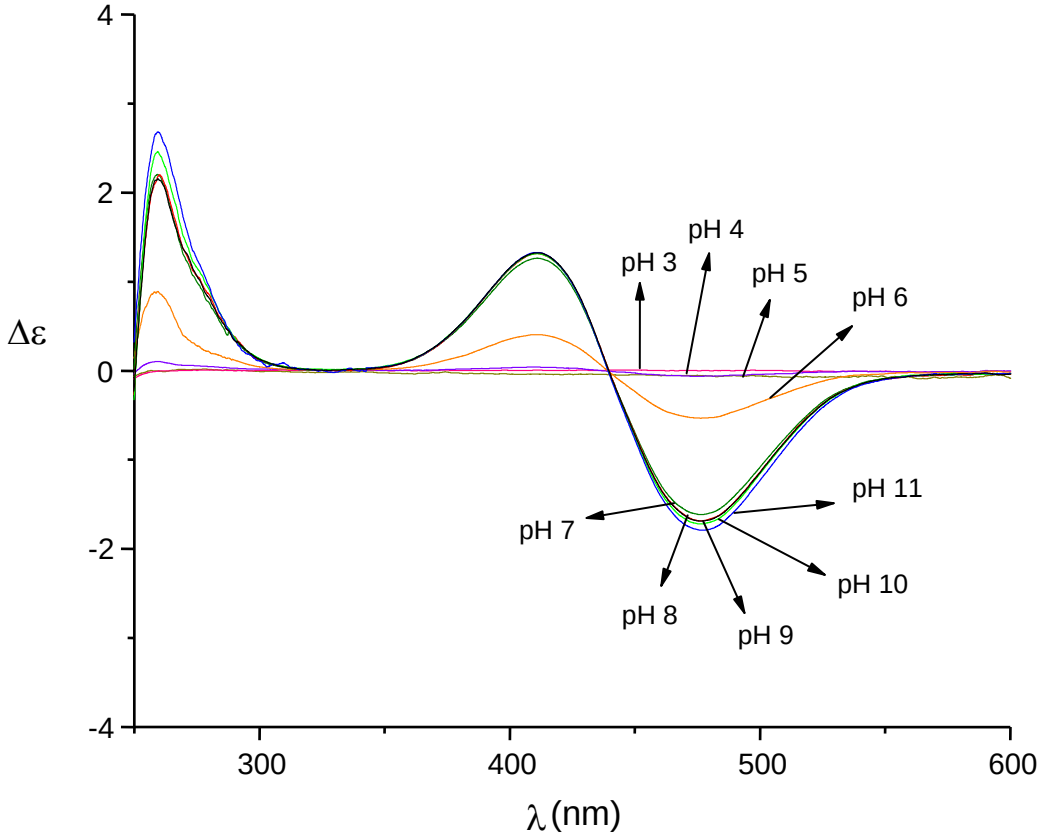
A CD plot Ni^{2+} – MAHHEQQHQA-NH_2



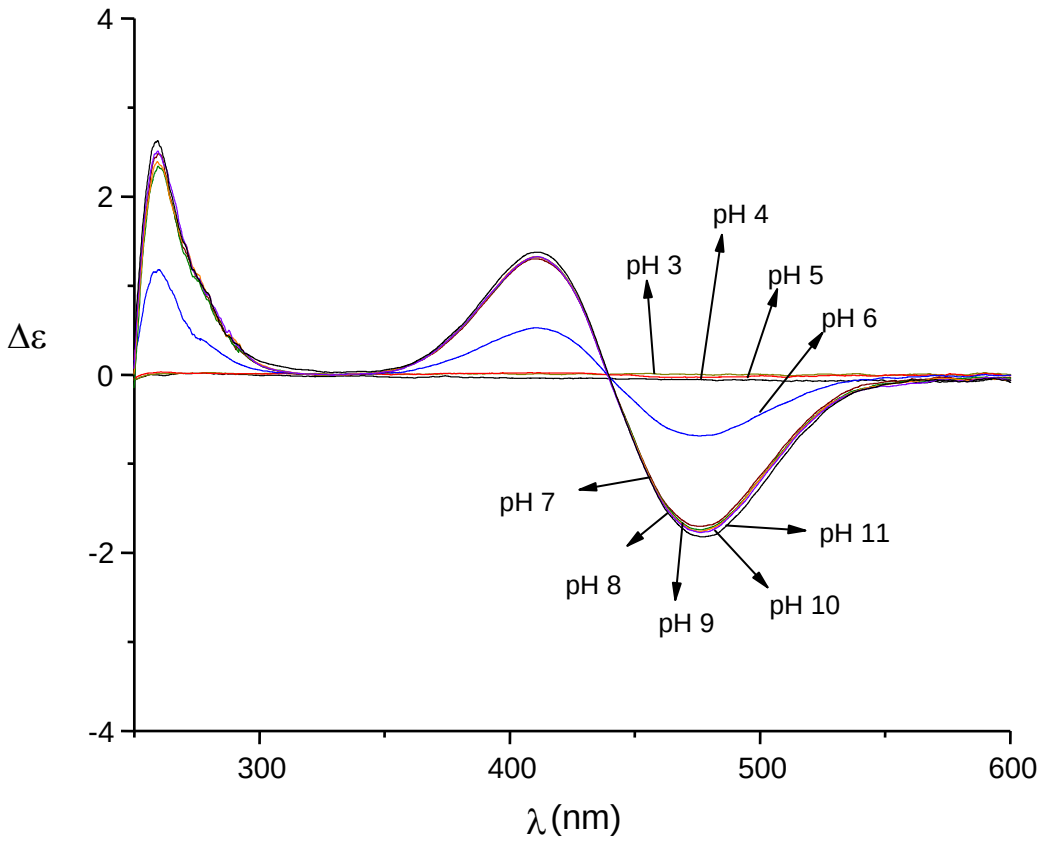
A CD plot Ni^{2+} – MAHHEQQ-NH_2



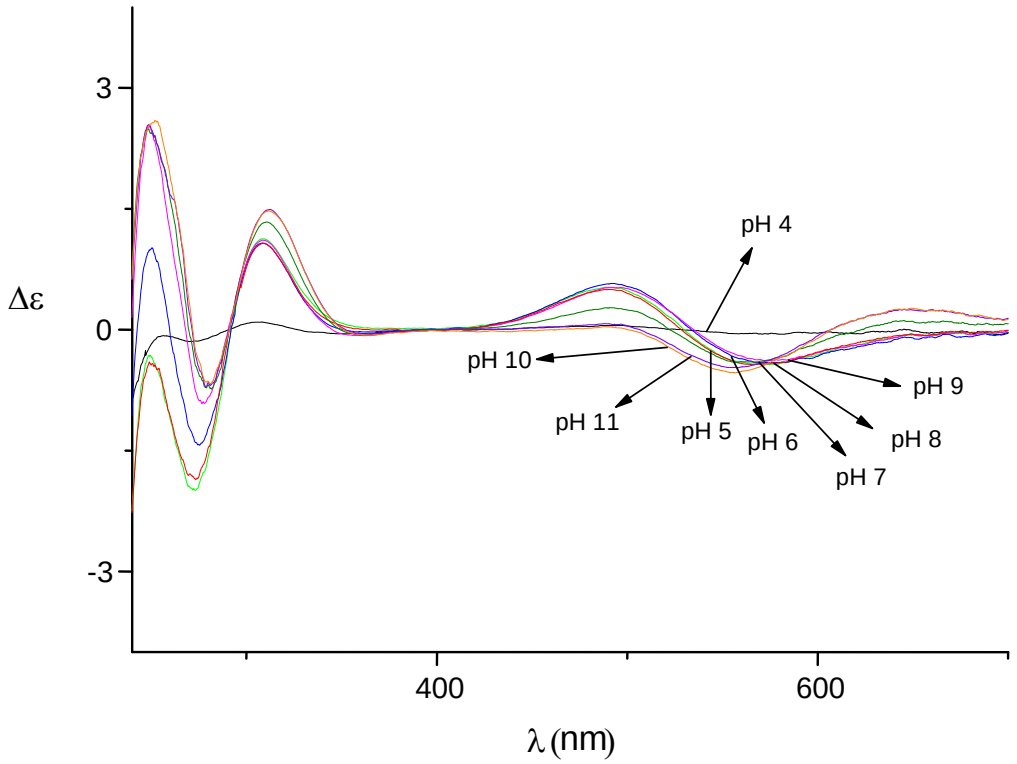
B CD plot Ni^{2+} – MAHHEEQ-NH_2



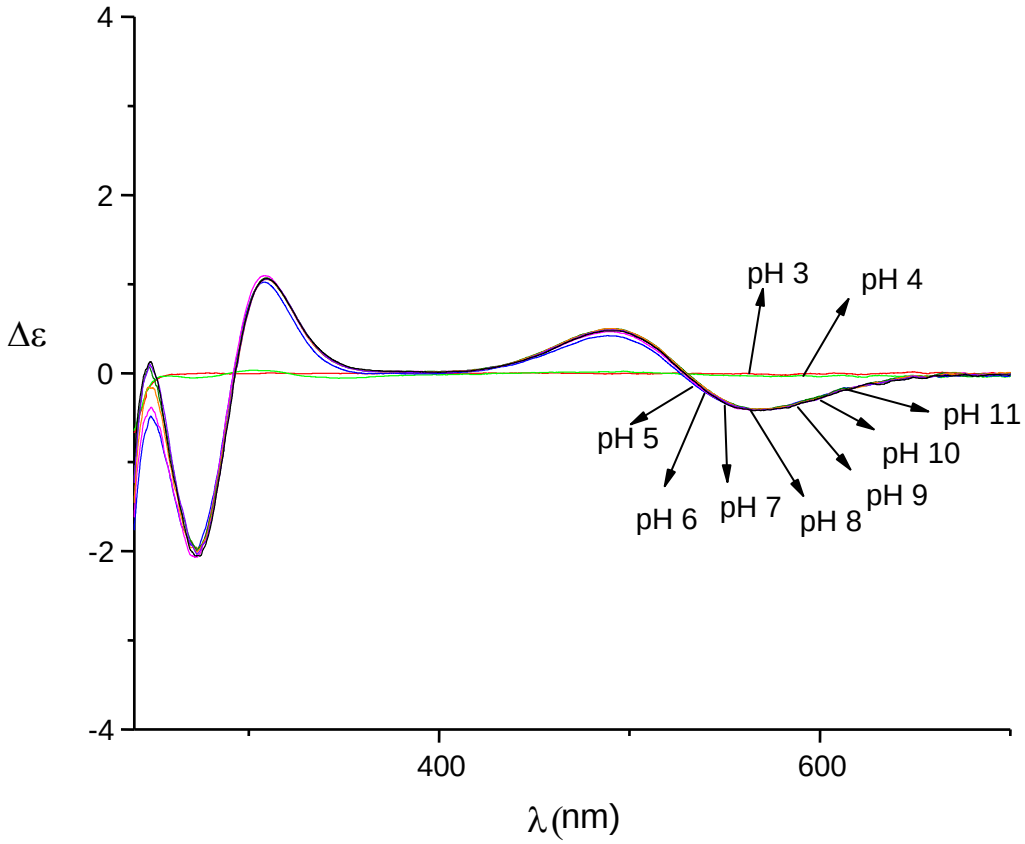
C CD plot Ni^{2+} – MAHHE-NH_2



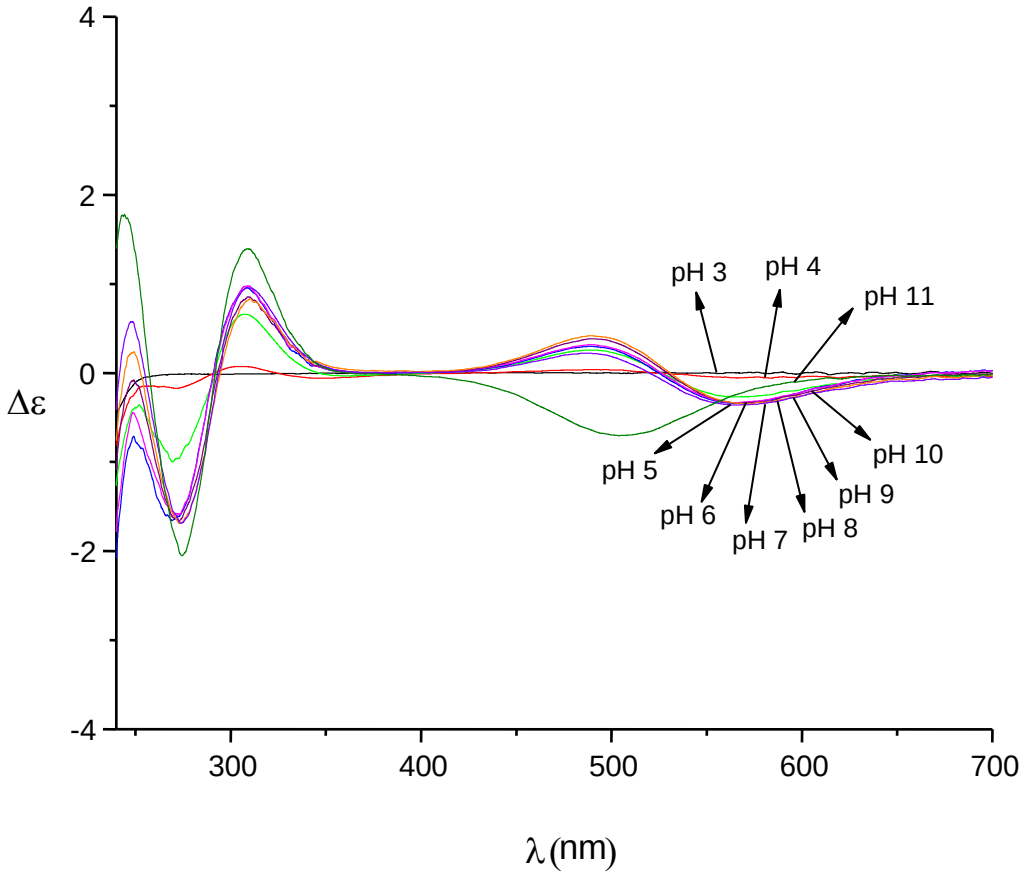
D CD plot Cu^{2+} – MAHHEQQHQA-NH_2



E CD plot Cu^{2+} – MAHHEQQ-NH_2



F CD plot Cu^{2+} – MAHHEEQ-NH_2



G CD plot Cu^{2+} – MAHHE-NH_2

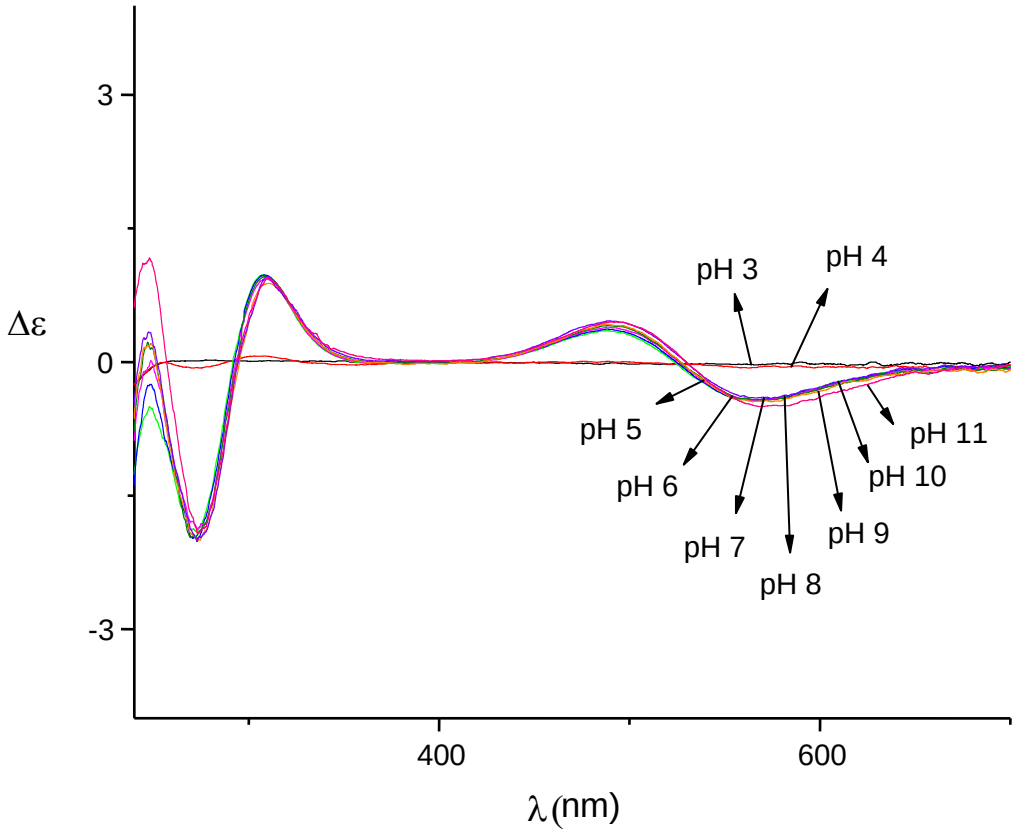
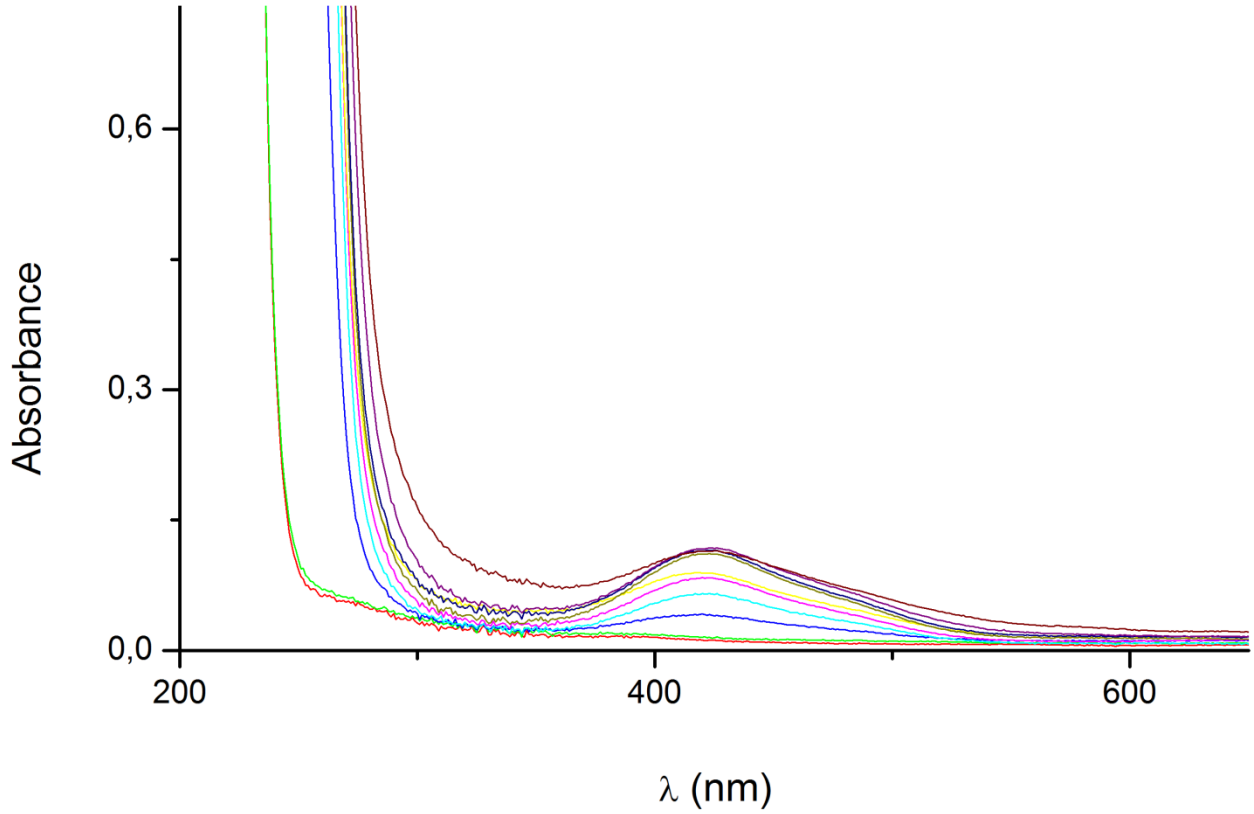
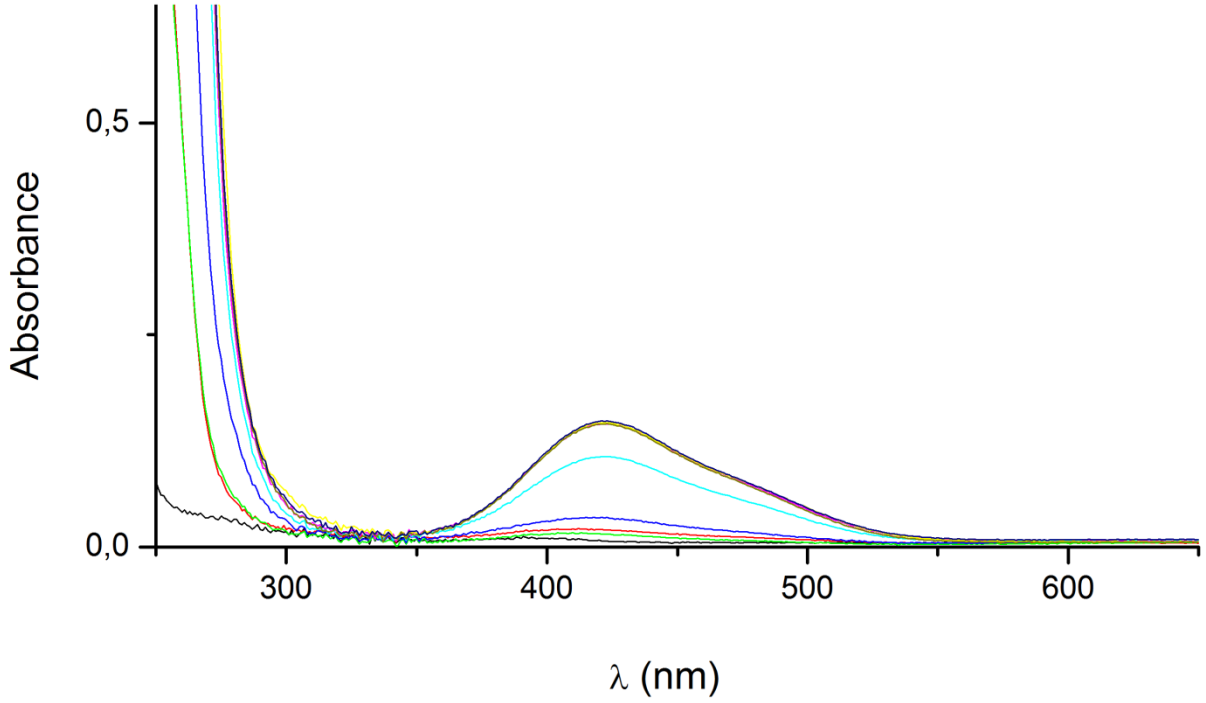


FIGURE S4. UV-Vis spectra of the studied systems. Metal : ligand ratio = 1:1.1, $[ligand]_{tot} = 10^{-3}$ M), I=0,1M (4mM HCl and 0.096M KCl), 298K. The studied pH ranges from 2 to 11. On all plots, the change of the spectral shape and intensity (together with potentiometric and circular dichroism data) suggest an albumine-like binding mode. A correlation between the species distribution and spectral parameters can be found in the tables; a wider description of this correlation is discussed in the main body of this paper.

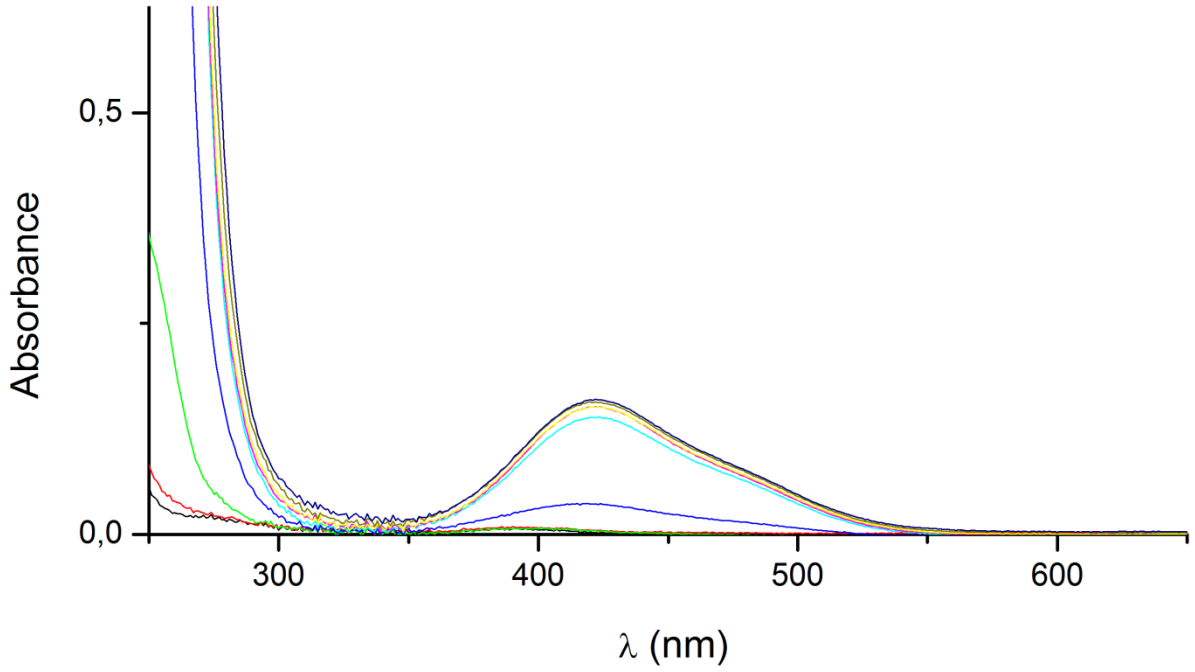
A UV-vis plot Ni^{2+} – MAHHEEQHQA-NH_2



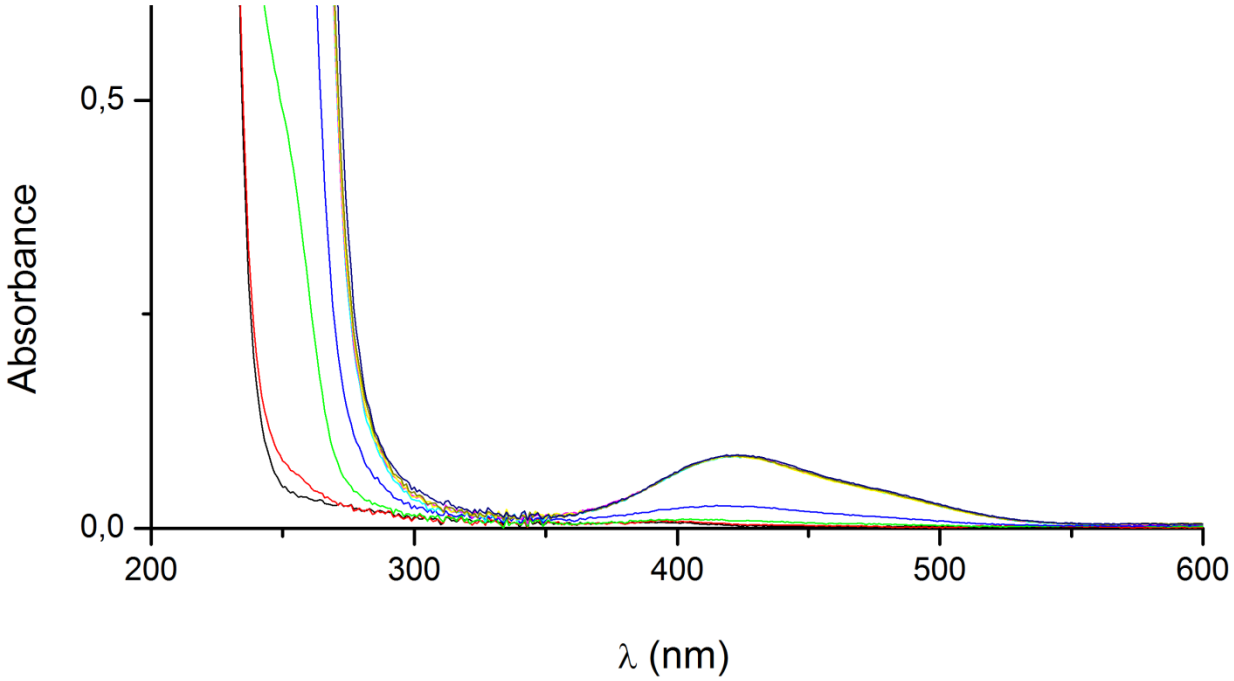
B UV-vis plot Ni^{2+}– MAHHEQQ-NH_2



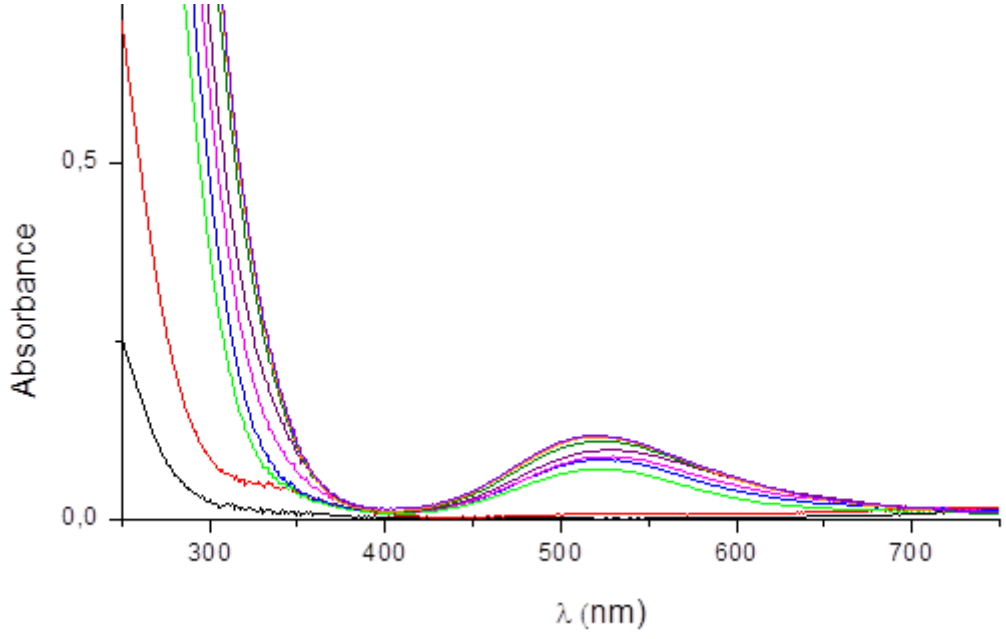
C UV-vis plot Ni^{2+} – MAHHEEQ-NH_2



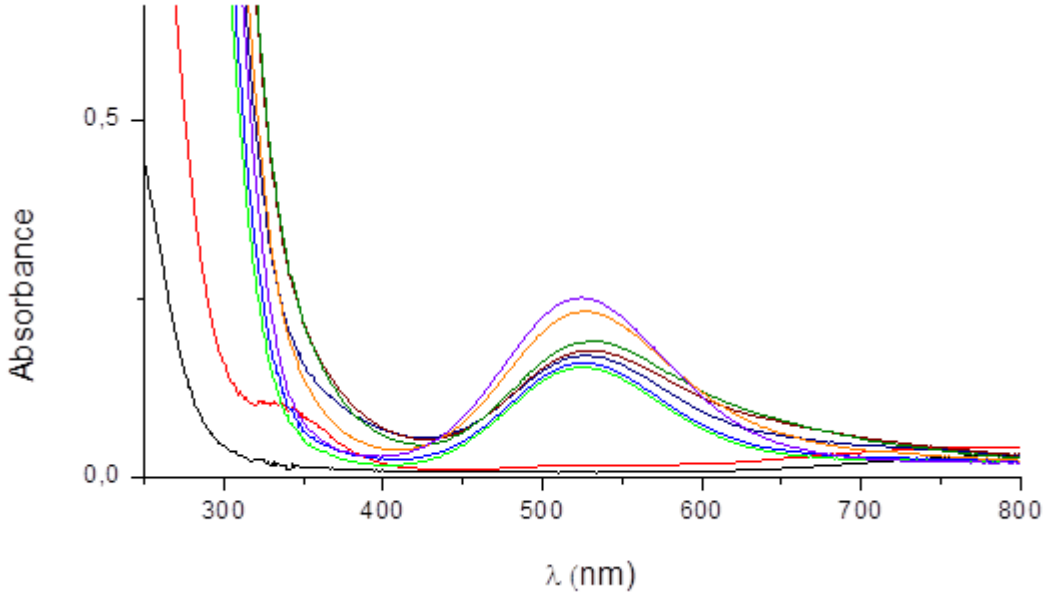
D UV-vis plot Ni^{2+} – MAHHE-NH_2



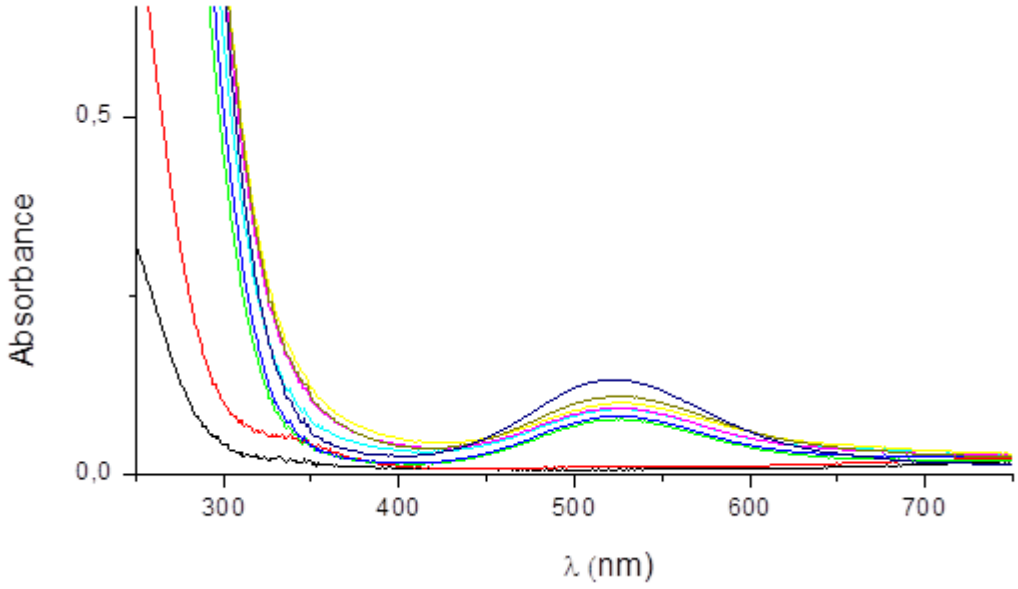
E UV-vis plot Cu^{2+}– MAHHEEQHQA-NH_2



F UV-vis plot Cu^{2+} – MAHHEQQ-NH_2



G UV-vis plot Cu^{2+} – MAHHEEQ-NH_2



H UV-vis plot Cu^{2+} – MAHHE-NH_2

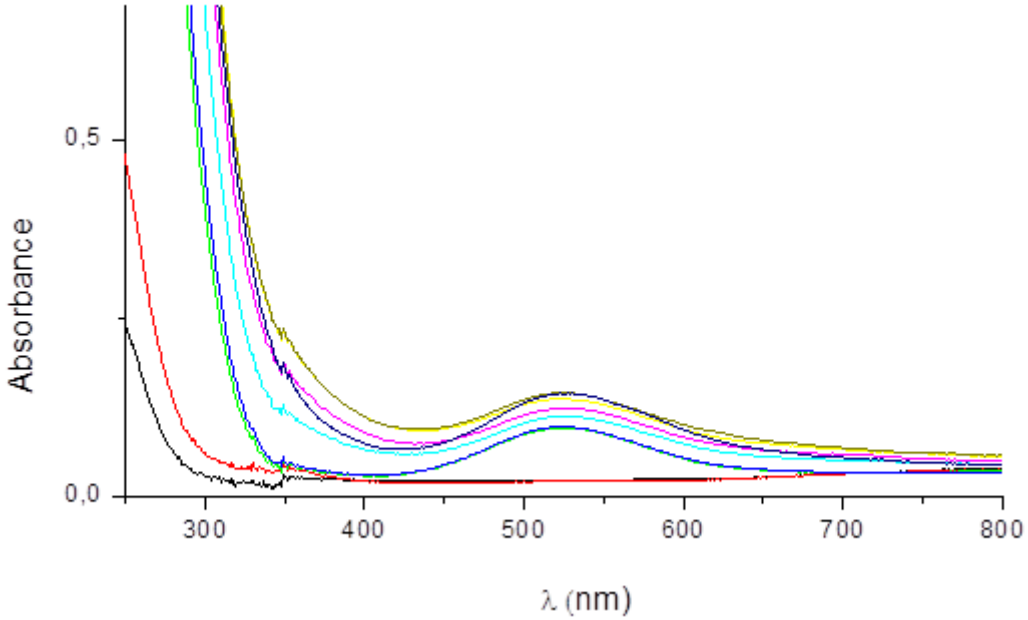
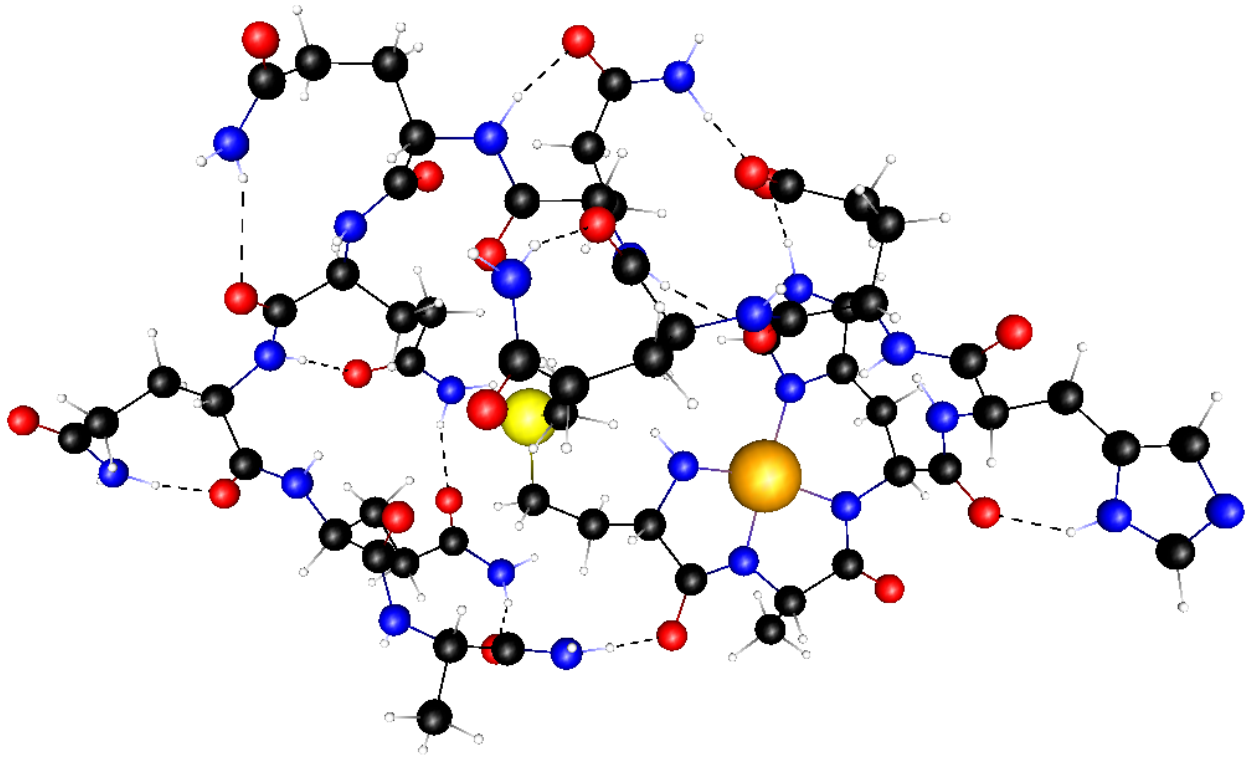
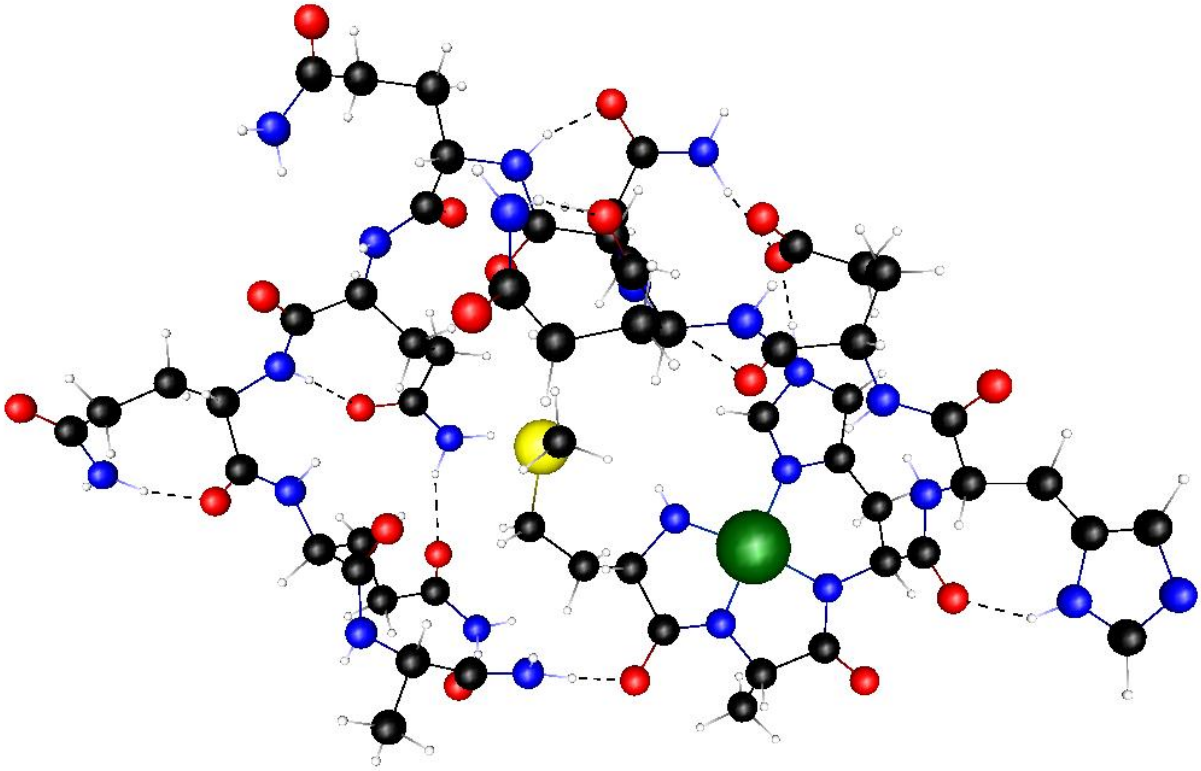


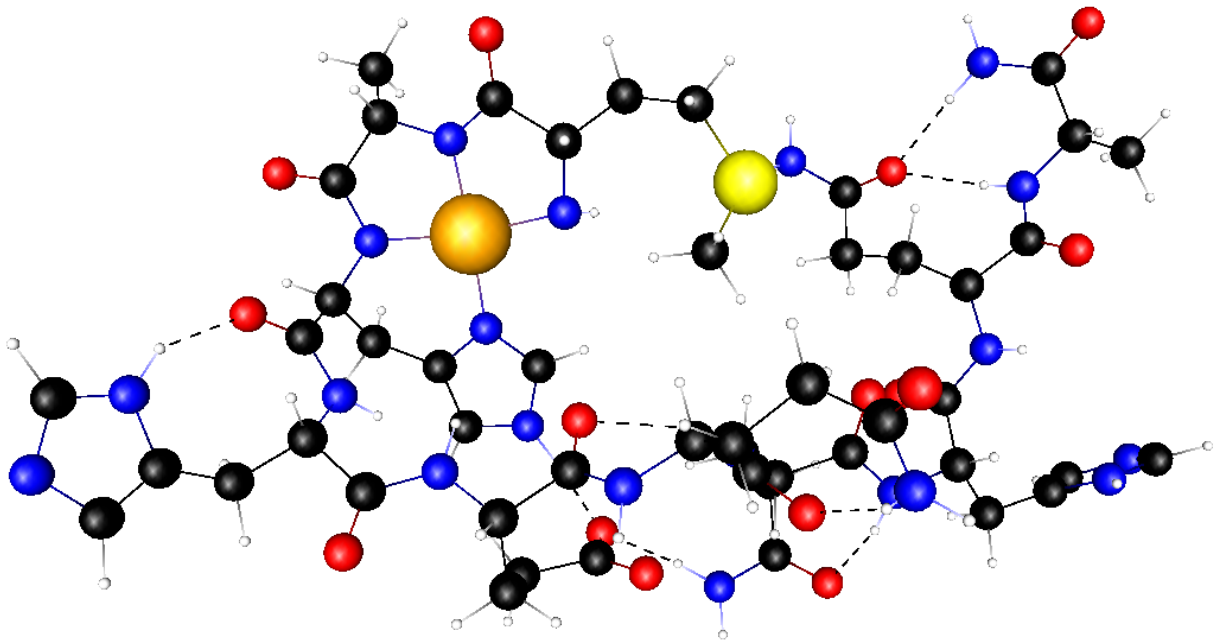
FIGURE S5. Fully optimized simulated structures of the Cu^{2+} and Ni^{2+} complexes discussed in the paper. Hydrogen bonds between glutamine residues are made visible. Copper – orange, nickel – green. All structures are signed below the appropriate figure with the metal and peptide sequence.



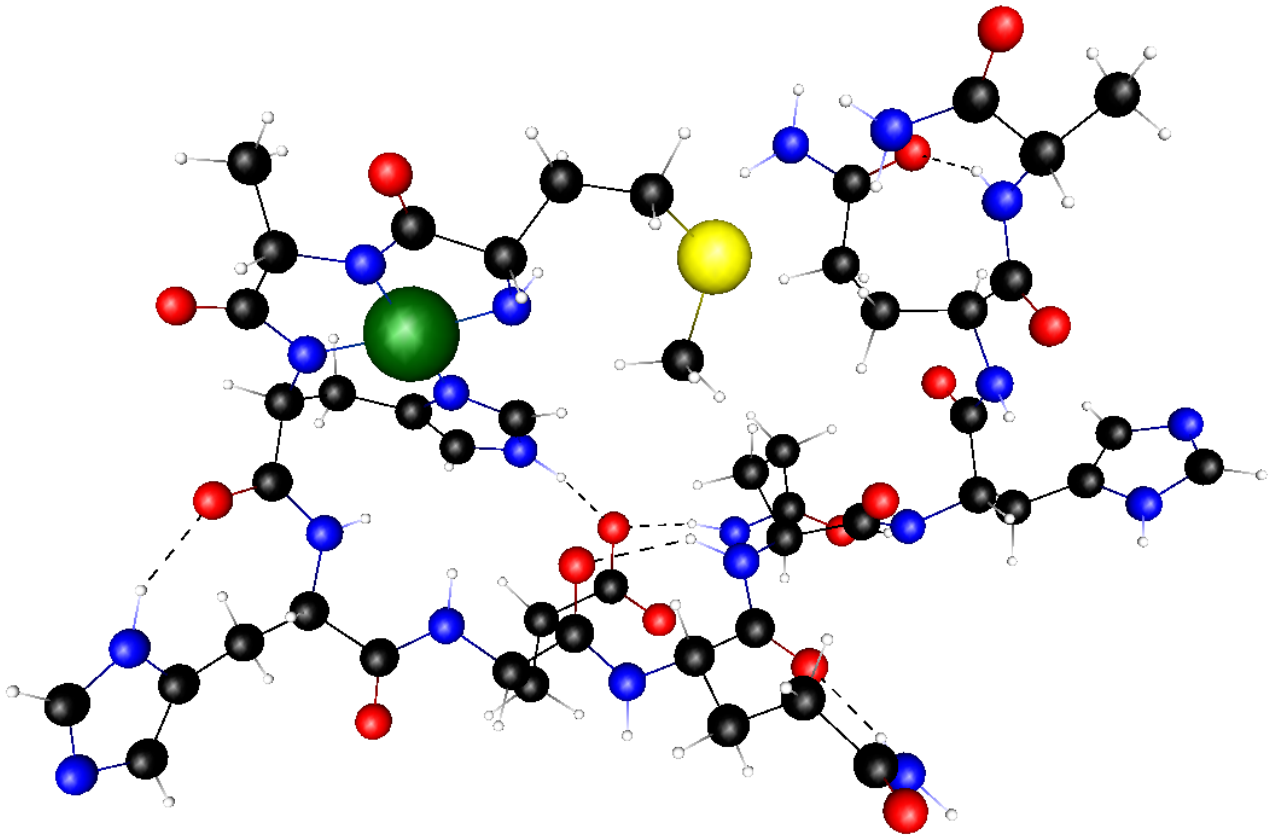
A Cu^{2+}-MAHHEEQQQQQQA-NH_2



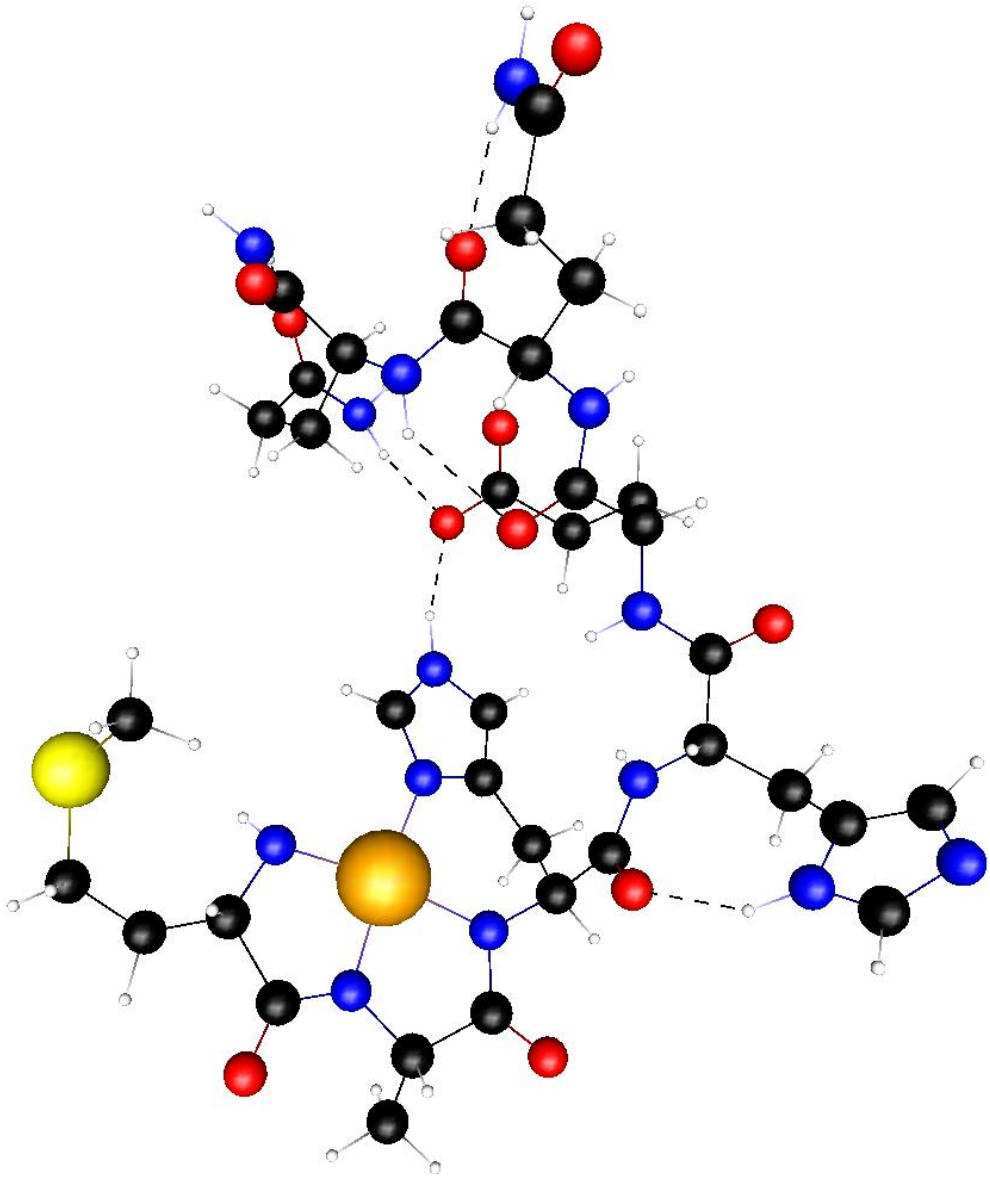
B Ni^{2+}-MAHHEEQQQQQQA-NH_2



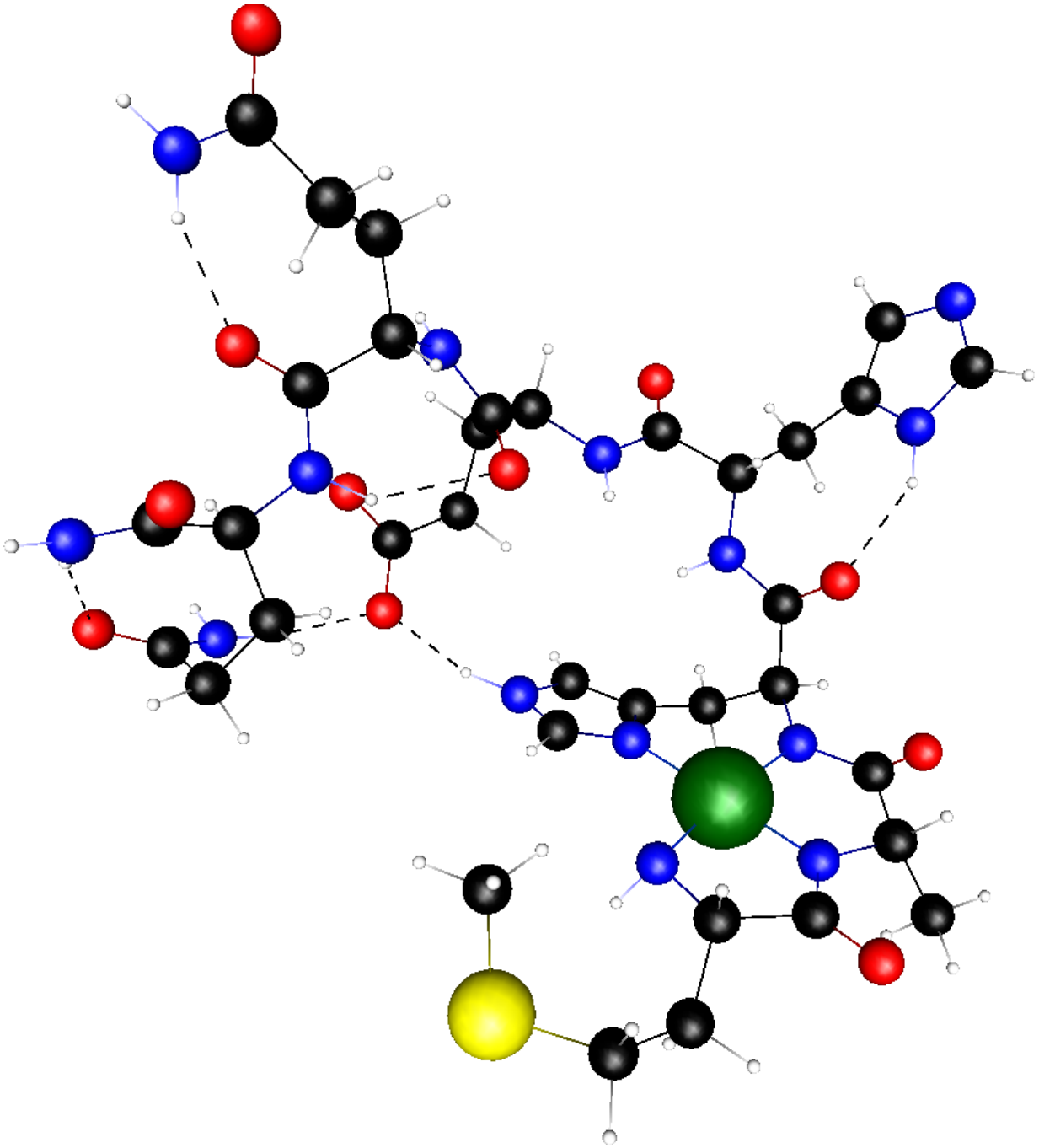
C Cu^{2+}-MAHHEQQHQA-NH_2



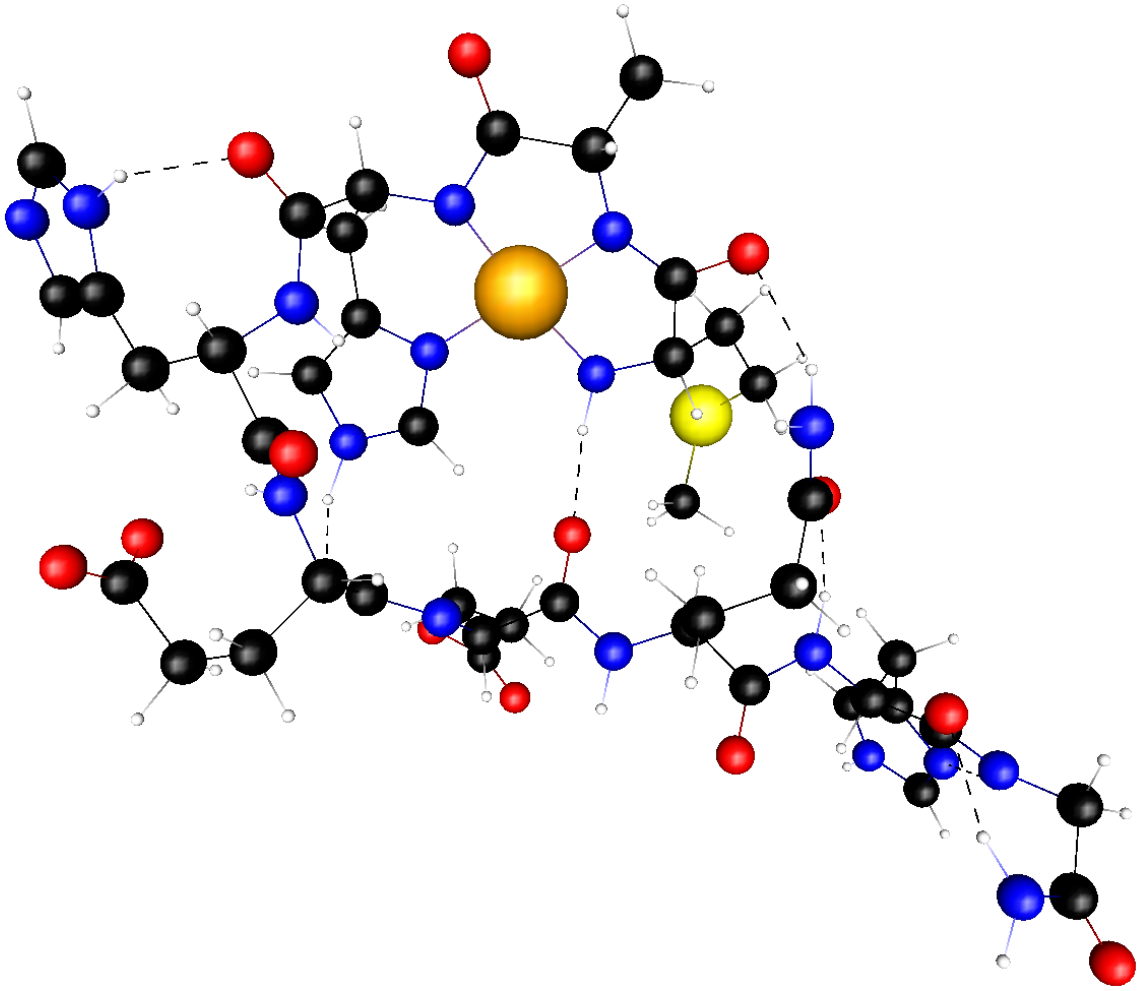
D Ni^{2+}-MAHHEQQHQA-NH_2



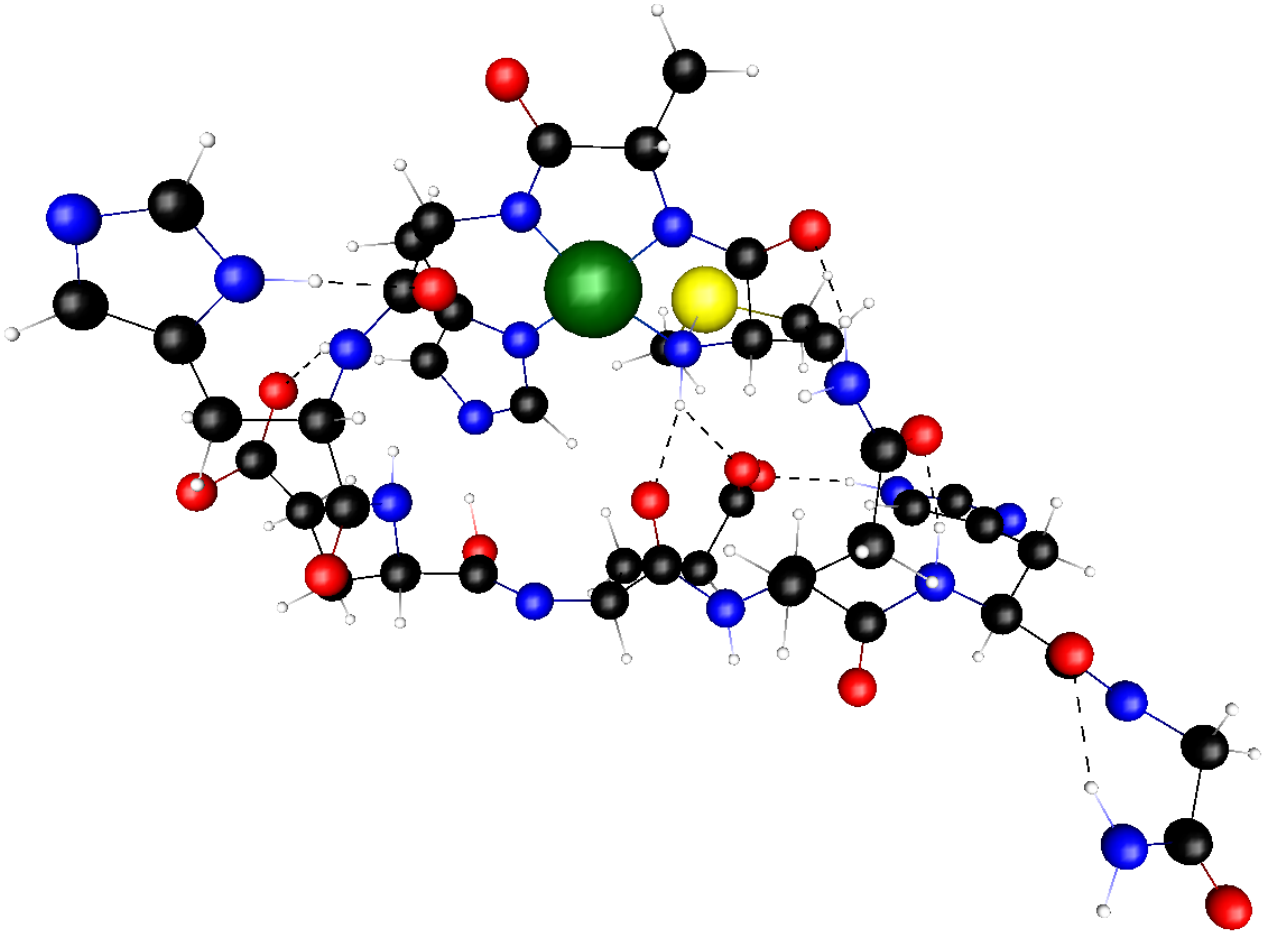
E Cu^{2+}-MAHHEQQ-NH_2



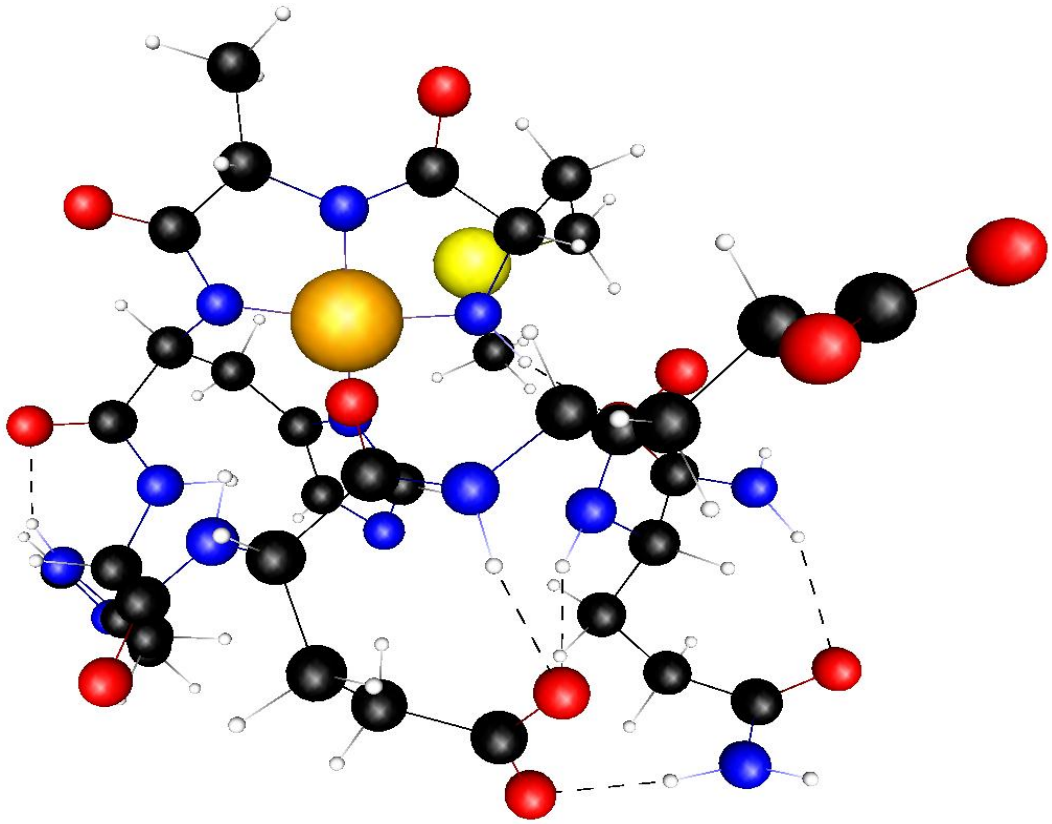
F Ni^{2+}-MAHHEQQ-NH_2



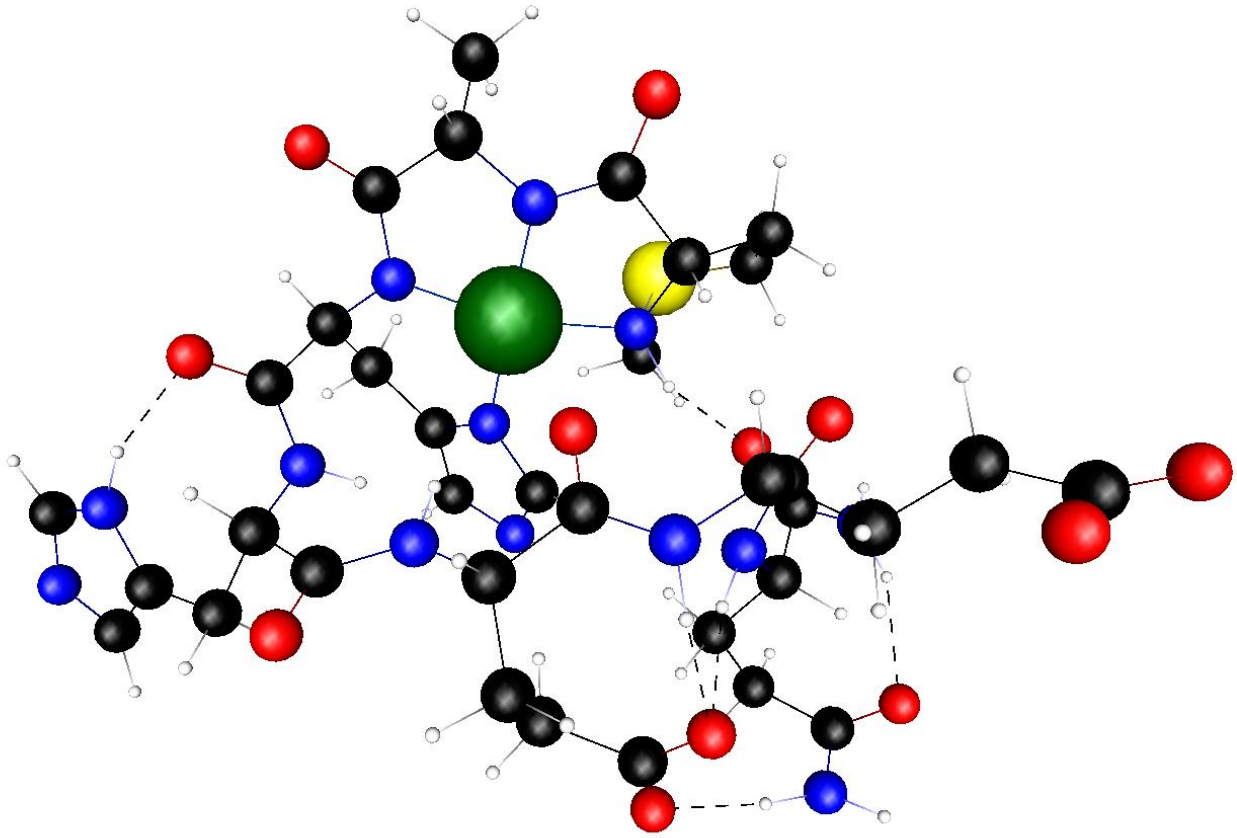
G Cu^{2+}-MAHHEEQHG-NH_2



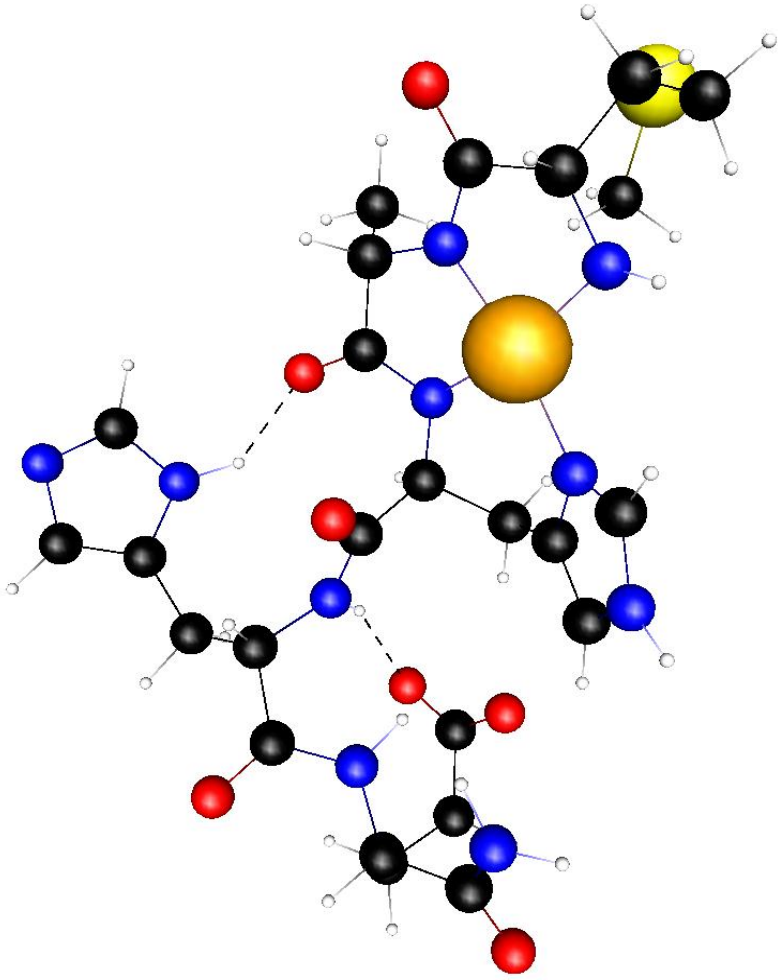
H Ni^{2+}-MAHHEEQHG-NH_2



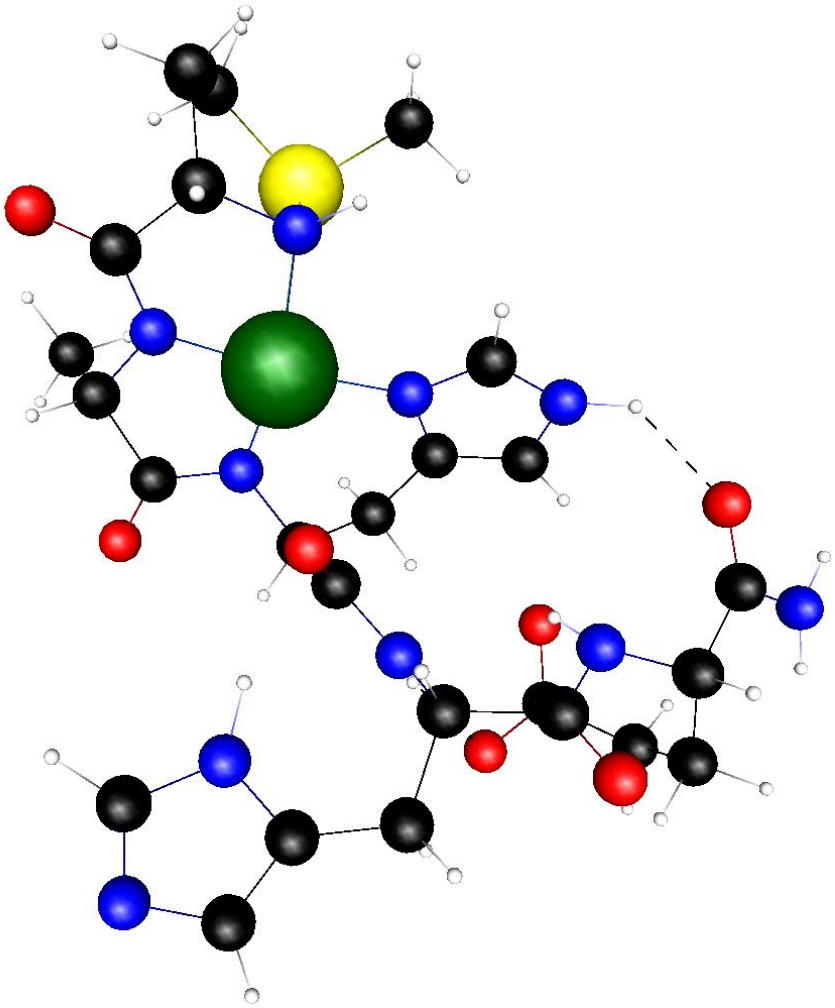
I Cu^{2+}-MAHHEEQ-NH_2



J Ni^{2+}-MAHHEEQ-NH_2



K Cu^{2+}-MAHHE-NH_2



L Ni^{2+}-MAHHE-NH_2