SUPPLEMENTARY INFORMATION

Metallacrowns as products of the aqueous medium self-assembly of histidinehydroxamic acid-containing polypeptides

*Marta Cal[a], , Aleksandra Kotynia[b], Łukasz Jaremko[c, d], Mariusz Jaremko[d], Marek Lisowski[a], Małgorzata Cebo[a] , Justyna Brasuń[b] and Piotr Stefanowicz[a]**

[a] Faculty of Chemistry, University of Wroclaw, Joliot-Curie 14, 50-383 Wroclaw, Poland

[b] Medical University of Wroclaw, Faculty of Pharmacy, Borowska 211A, 50-556 Wroclaw, Poland

[c] Max Planck Institute for Biophysical Chemistry and German Center for Neurodegenerative Diseases, Am Fassberg 11, 37077 Goettingen, Germany

[d] Department for NMR-based Structural Biology, Max Planck Institute for Biophysical Chemistry, Am Fassberg 11, 37077, Goettingen, Germany

Table S1. The comparison of experimental and calculated value of *m/z* for the most abundant monoisotopic peaks. In this table the data from **Figure 3** are collected.

Peptide	z	experimental *m/z* value	calculated *m/z* value	elemental formula of complex	Absolute error [Da]	Relative error [ppm]
Ac-KLH-NHOH	2+	1061.8307	1061.8305	C80H136N28O20Cu5	0.0002	0.19
	3+	708.2250	708.2225	C80H137N28O20Cu5	0.0025	3.53
	4+	531.4191	531.4189	C80H138N28O20Cu5	0.0002	0.38

Table S2. Comparison of k_i values of Ac-KLH-NHOH and its complex with Cu(II) ions as a function of pH.

pH	Studied system $k \times 10^4$ [h^{-1}]	
	peptide	complex
5.2	2.0	-1.9
7.2	143.3	-2.7
7.3	168.0	0.4
8.2	400.2	2.4
8.3	417.3	3.3

I. The mass spectrometry

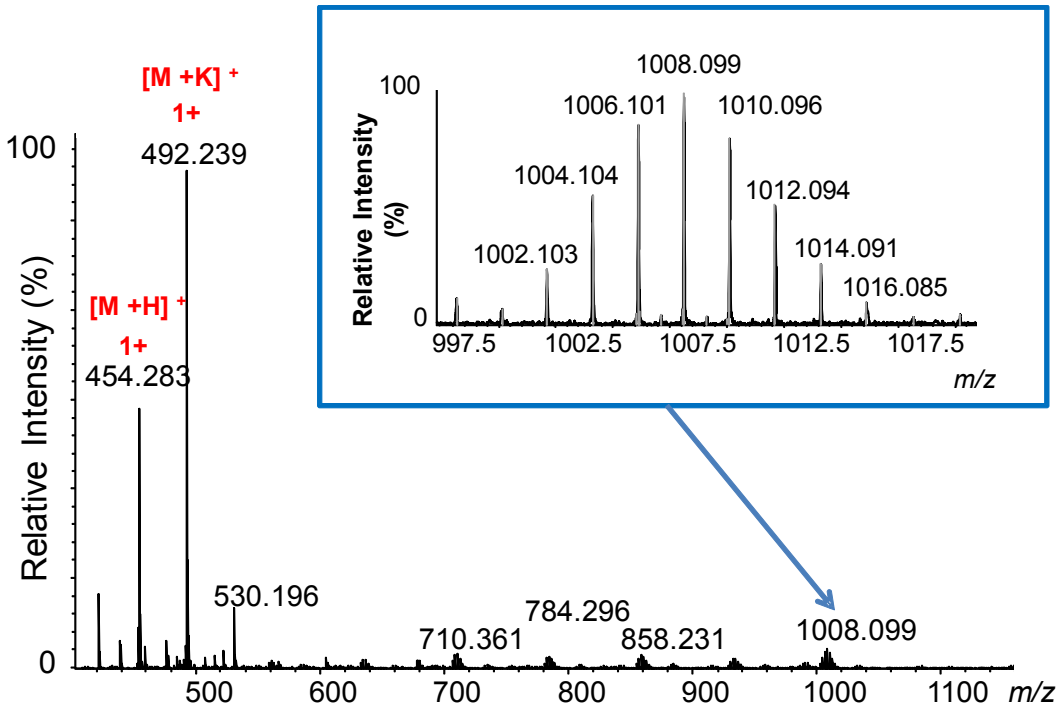

Figure S 1. The mass spectrum recorded for Ac-KLH-NHOH and Cu^{2+} at pH 10.5.

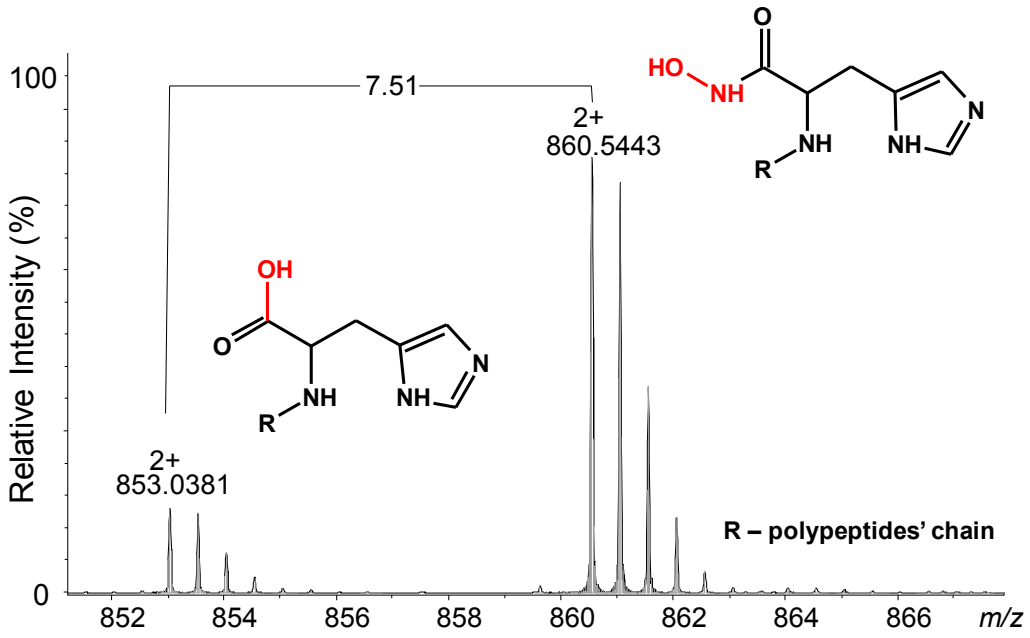

Figure S 2. The mass spectrum recorded for [AD]-NHOH after 20 min incubation at pH 9.5. The signal of *m/z* 860.5443 corresponds to the peptide with hydroxamic acid (marked in red color) and the signal of *m/z* 853.0381 corresponds to the peptide with the carboxylic group instead of the hydroxamic acid one.

According to our preliminary experiments, the hydrolysis depends on the sequences of peptides and histidine strongly improves this process.

II. Circular dichroism

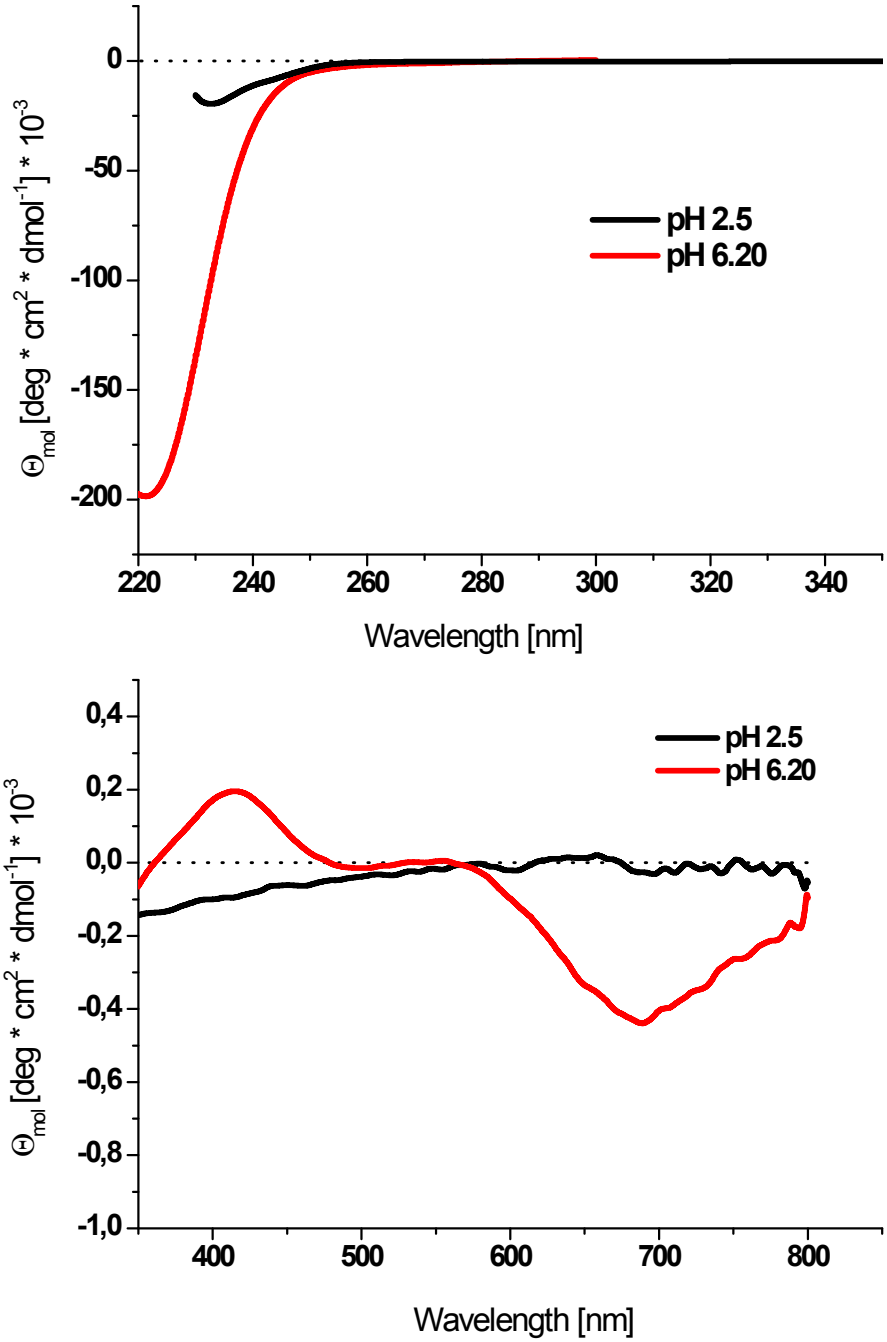

Figure S 3. Representative CD spectra registered for Cu(II)–[AH]-NHOH at the 0.8:1 metal:ligand ratio: $C_{Cu(II)}$ = 0.80×10^{-3} M. The CD spectra are shown in two ranges for a better presentation of the bands of different molar ellipticity values.

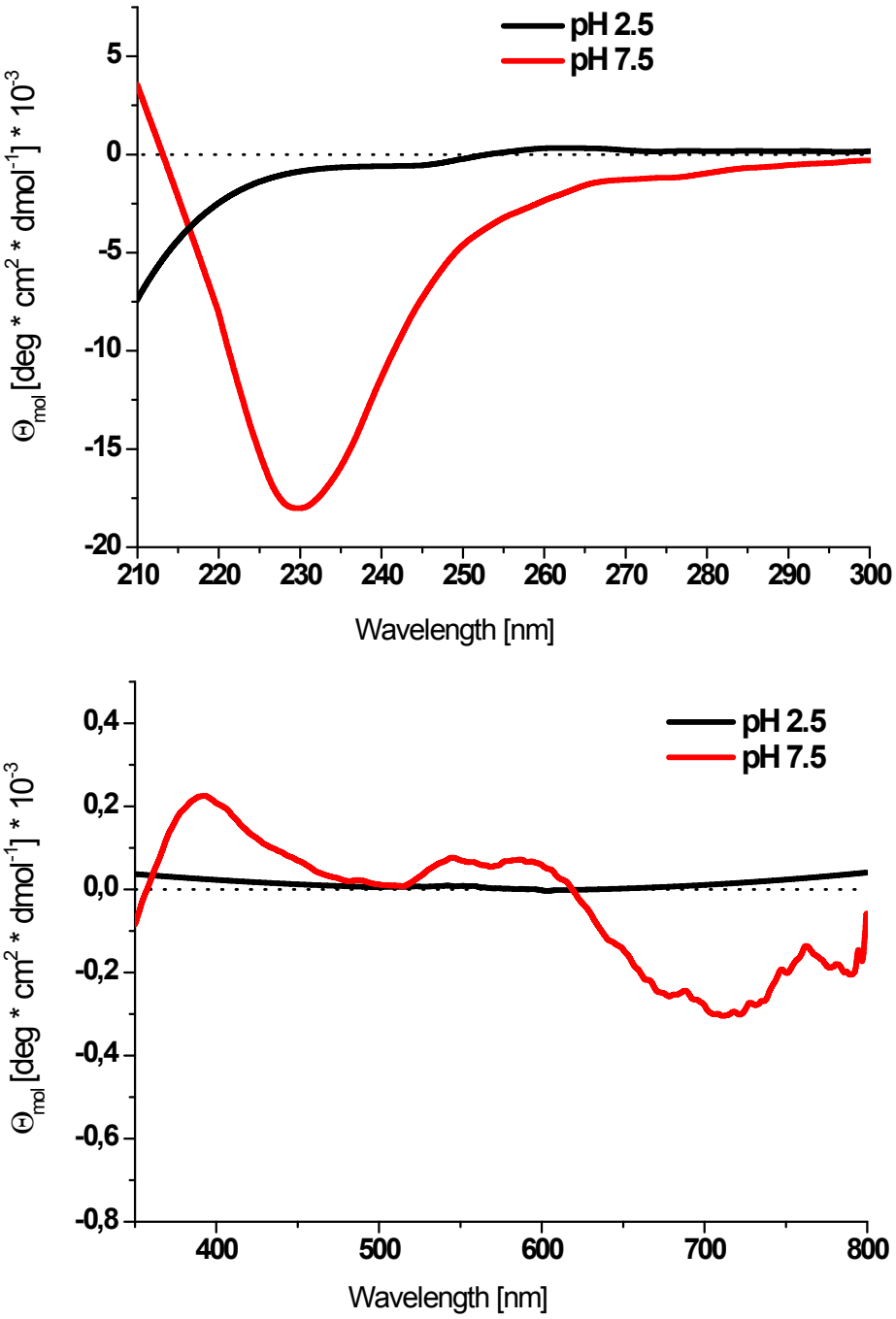

Figure S 4. Representative CD spectra registered for Cu(II)–Ac-KLH-NHOH as a function of pH at the 0.8:1 metal:ligand ratio: $C_{Cu(II)}$ = 0.80×10^{-3} M. The CD spectra are shown in two ranges for a better presentation of the bands of different molar ellipticity values.