

Electronic Supplementary Information

The role of methylation in the copper(II) coordination properties of a His-containing decapeptide

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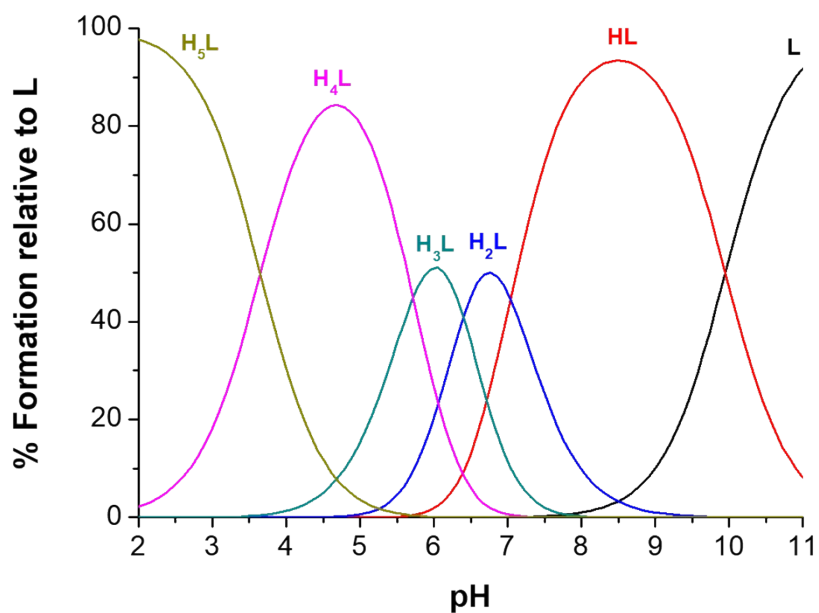


Figure S1. Species distribution diagram for the O_{NMe} -Asp peptide at 1.0×10^{-3} M concentration, 298.2 K and $I = 0.10$ M KNO_3 ($L = O_{NMe}$ -Asp).

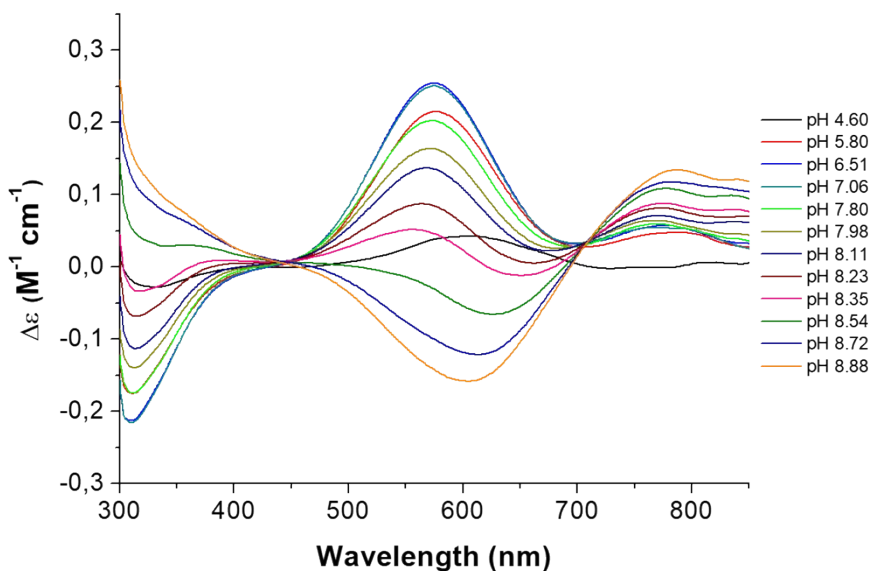


Figure S2. CD spectra of the copper(II) complexes formed with the O_{NMe} -Asp peptide in a 1:1 ratio (1.0×10^{-3} M) at different pH values, 0.1 M NaCl and 298.2 K.

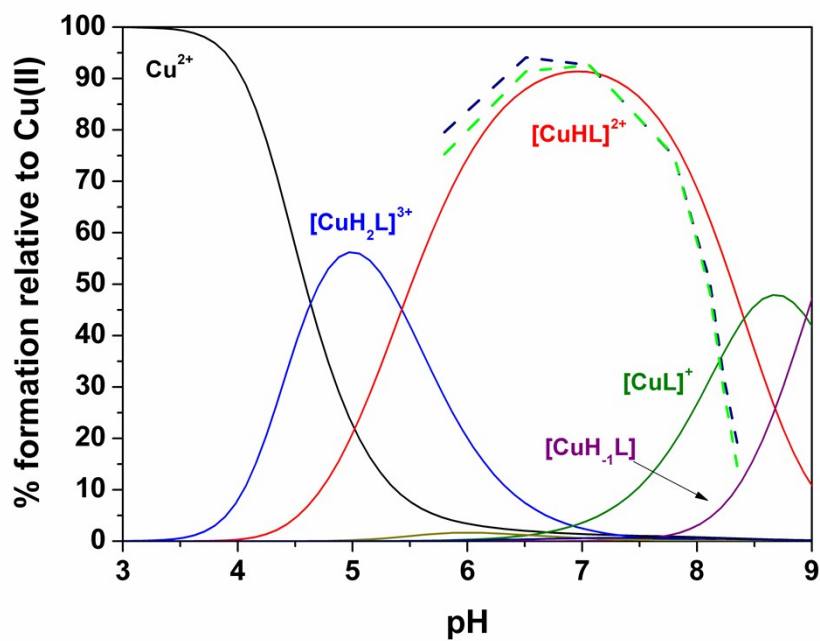


Figure S3. Species distribution diagram for the copper(II) complexes of $L = O_{\text{NMe}}\text{-Asp}$ ($C = 1.0 \times 10^{-3} \text{ M}$) with 1 equiv of $\text{Cu}(\text{NO}_3)_2$ at 298.2 K and $I = 0.10 \text{ M KNO}_3$. Dashed lines correspond to normalized molar circular dichroism absorption at 575 nm (dark-blue) and 310 nm (green).

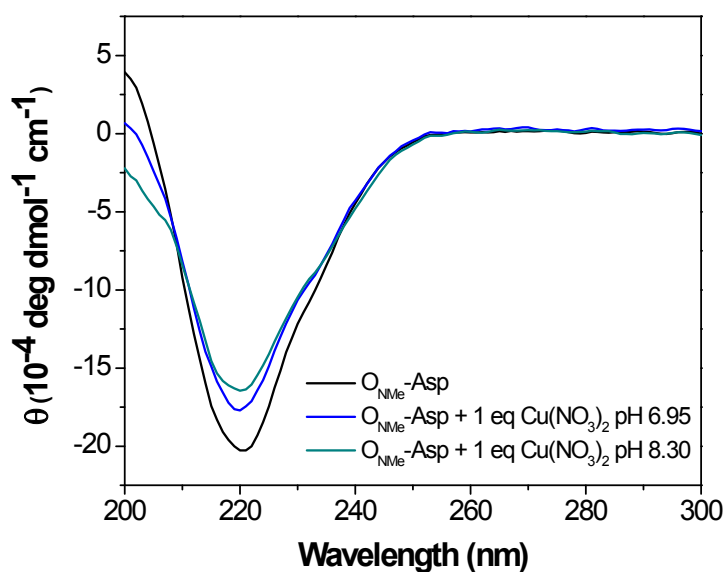


Figure S4. Far-UV CD spectra of the $O_{NMe}\text{-Asp}$ peptide (0.1×10^{-3} M) in the absence and presence of 1 equivalent of Cu^{2+} ions at pH 6.95 ($[\text{CuH}(O_{NMe}\text{-Asp})]^{2+}$) and 8.30 ($[\text{Cu}(O_{NMe}\text{-Asp})]^+$) (0.1 M NaCl).

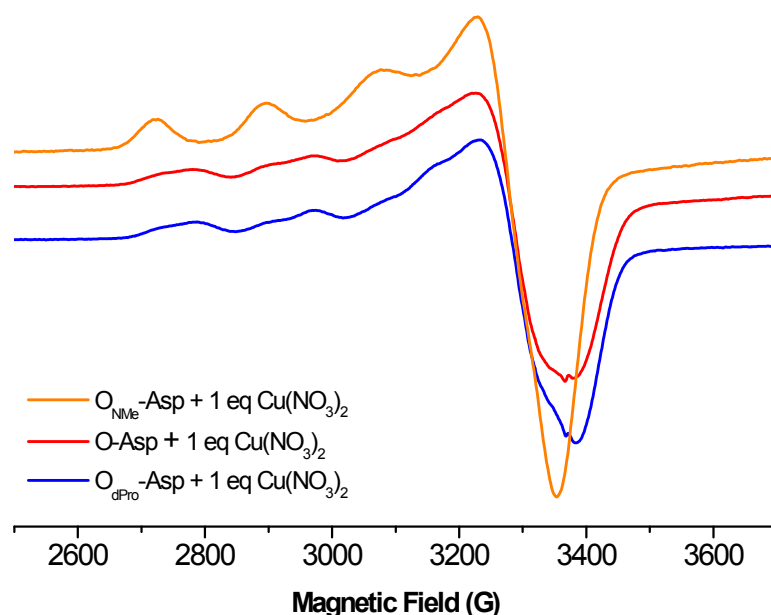


Figure S5. X-band EPR spectra recorded at 120 K of solutions containing the $O\text{-Asp}$, $O_{dPro}\text{-Asp}$ and $O_{NMe}\text{-Asp}$ peptides (1×10^{-3} M) and 1 equivalent of Cu^{2+} ions ($\text{Cu}(\text{NO}_3)_2$) in 10 mM HEPES buffer at pH 8.30.

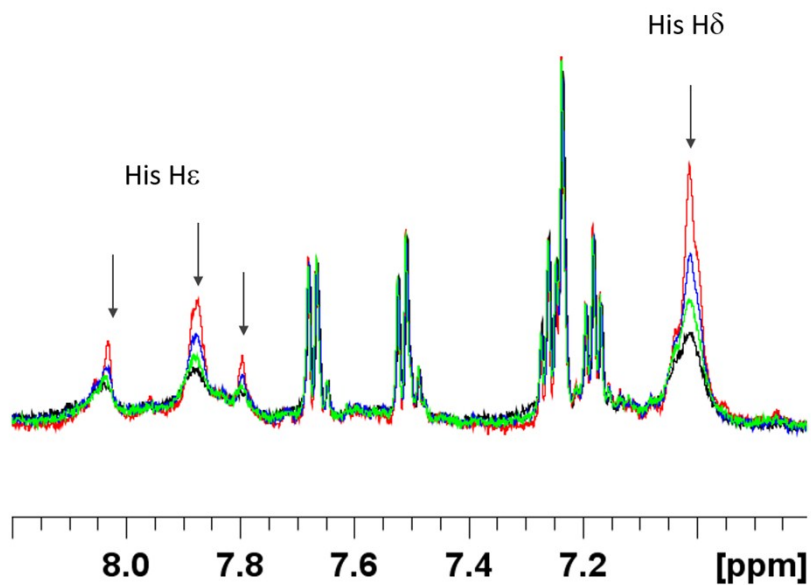


Figure S6. Superimposition of ¹H 1D NMR spectra of O_{NMe}-Asp in absence (red) and in presence of 0.02 (blue), 0.05 (green) and 0.1 (black) equivalents of Cu²⁺.

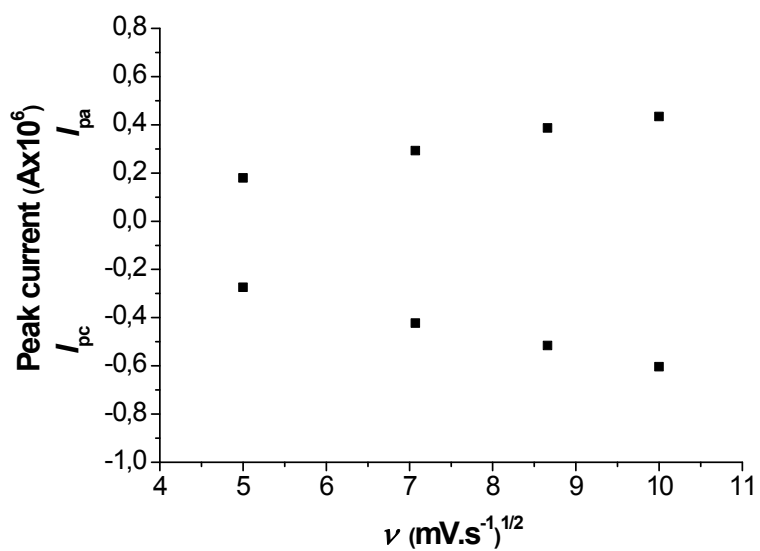


Figure S7. Variation of the anodic and cathodic peak currents of the $[\text{CuH}(\text{O}_{\text{NMe}}\text{-Asp})]^{2+}$ complex (5.0×10^{-4} M) with the square root of the scan rate. Media: 0.10 M HEPES buffer (pH 7.0) and 0.10 M KNO_3 as supporting electrolyte.

Table S1: EPR parameters for the copper(II) complexes of O_{NMe}-Asp, O-Asp, O_{DPro}-Asp and C-Asp (1×10⁻³ M) at different pH values.

Peptides	pH	Species, (%)	g_1	g_2	g_3	$A_1(\times 10^{-4}\text{cm}^{-1})$	$A_2(\times 10^{-4}\text{cm}^{-1})$	$A_3(\times 10^{-4}\text{cm}^{-1})$
O _{DPro} -Asp + 1 eq Cu(NO ₃) ₂	6.0	[CuHO _{DPro} -Asp] ²⁺ , 100%	2.080	2.040	2.270	17.8	5.3	181.5
	8.3	Species 1 ^[a] , ND	-	-	2.252	< 28 ^[b]	< 28 ^[b]	184.0
	8.3	Species 2 ^[a] , ND	-	-	2.200	< 28 ^[b]	< 28 ^[b]	191.0
O-Asp + 1 eq Cu(NO ₃) ₂	6.0	[CuHO-Asp] ²⁺ , 100%	2.070	2.040	2.271	21.6	6.4	181.7
	8.3	Species 1, 48%	2.047	2.047	2.260	< 28 ^[b]	< 28 ^[b]	172.0
	8.3	Species 2, 52%	2.060	2.060	2.199	< 28 ^[b]	< 28 ^[b]	179.0
O _{NMe} -Asp + 1 eq Cu(NO ₃) ₂	7.0	[CuHO _{NMe} -Asp] ²⁺ , 100%	2.050	2.034	2.268	< 28 ^[b]	< 28 ^[b]	175.8
	8.3 ^[c]	Species 1	2.050	2.034	2.268	< 28 ^[b]	< 28 ^[b]	175.8

^[a] EPR parameters could not be simulated, these are manually extracted parameters. ^[b] Simulation could not precisely determine the A value. ^[c] A second species was detected at pH 8.3, however, parameters could not be extracted. ND: Not Determined.

Table S2. E_{pc} , E_{pa} and $(E_{pc} + E_{pa})/2$ values for the $[\text{CuH}(\text{O}_{\text{NMe}}\text{-Asp})]^{2+}$ complex at different scan rates.^a

Scan rates (mV/s)	E_{pc} (V)	E_{pa} (V)	ΔE_p (V)	$(E_{pc} + E_{pa})/2$ (V)
25	0.014	0.526	0.512	0.270
50	0.004	0.556	0.552	0.280
75	-0.006	0.526	0.532	0.260
100	-0.016	0.586	0.602	0.285

^(a) A three-electrode configuration cell was used with a glassy carbon electrode as a working electrode, a platinum wire as auxiliary electrode and as reference a Ag/AgCl electrode.

Table S3. Anodic and cathodic peak currents of the $[\text{CuH}(\text{O}_{\text{NMe}}\text{-Asp})]^{2+}$ at different scan rates.

Scan rates (mV/s)	Peak currents (A)	
	$I_{pa}(\times 10^6)$	$I_{pc}(\times 10^6)$
25	1.798	-2.739
50	2.923	-4.225
75	3.867	-5.159
100	4.337	-6.040