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Coordination of Cu^{2+} and Ni^{2+} with the Histone Model Peptide of H2B N-terminal tail (1-31 residues): A Spectroscopic Study.

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Supporting Information

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Table S1. Acquisition parameters of NMR experiments performed on $H2B_{1-31}$ at 298K.

Experiments	Acquired data points (nucleus)			Spectral width (ppm)		
	t_1	t_2	t_3	F_1	F_2	F_3
[^{1}H, ^{1}H]-TOCSY[a][b]	2048 (^{1}H)	672 (^{1}H)	-	10 (^{1}H)	10 (^{1}H)	-
[^{1}H, ^{1}H]-NOESY[a][b]	2048 (^{1}H)	640 (^{1}H)	-	11 (^{1}H)	11 (^{1}H)	-
[^{1}H, ^{13}C]-HSQC[a][b][c]	1024 (^{1}H)	512 (^{13}C)	-	11 (^{1}H)	80 (^{13}C)	-
[^{1}H, ^{15}N]-HSQC[a]	1024 (^{1}H)	256 (^{15}N)	-	12 (^{1}H)	40 (^{15}N)	-
HNHA[a]	128 (^{1}H)	16 (^{15}N)	1024 (^{1}H)	13 (^{1}H)	37 (^{15}N)	13 (^{1}H)

[a] Data acquired on a 700 spectrometer, equipped with a triple resonance TXI Z-GRAD 5 mm.

[b] Data acquired on a 600 MHz spectrometer equipped with a triple resonance TXI Z-GRAD 5 mm and TXI Z-GRAD with ATMM 5 mm probe, for the Ni^{2+}-free and bound $H2B_{1-31}$ spectra, respectively.

[c] Data acquired on a 400 MHz spectrometer equipped with a triple resonance TXI BBO 5 mm probe (for Cu^{2+}-$H2B_{1-31}$ complexes).

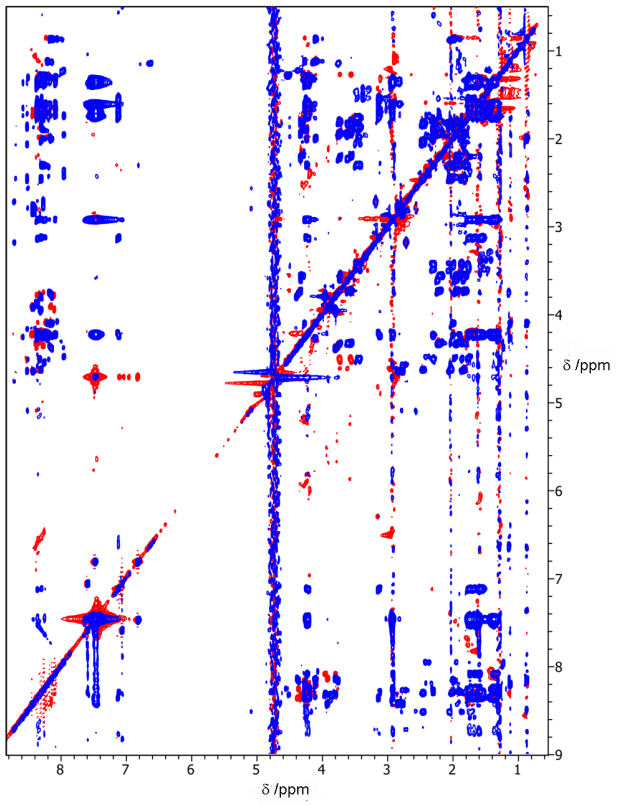

Figure S1. Overlaid NOESY (red) and TOCSY (blue) spectra of $H2B_{1-31}$ at pH 2, 298 K.

Table S2. Resonance assignments for $H2B_{1-31}$ at pH 2, 298 K (ppm related to TMS).

Residue	Atom	δ/ppm	Residue	Atom	δ/ppm	Residue	Atom	δ/ppm
Pro1	$^{1}H\alpha$	4.50	Pro3	$^{1}H\gamma_2$	1.93	Lys5	$^{13}C\gamma$	22.0
	$^{1}H\beta_2$	2.30		$^{1}H\gamma_3$	1.83		$^{13}C\delta$	26.3
	$^{1}H\beta_3$	1.98		$^{13}C\alpha$	60.39		$^{13}C\varepsilon$	39.3
	$^{1}H\delta_2$	3.46		$^{13}C\beta$	29.35	Ser6	$^{1}H_N$	8.16
	$^{1}H\delta_3$	3.42		$^{13}C\gamma$	29.31		$^{1}H\alpha$	4.36
	$^{1}H\gamma_2$	1.88		$^{13}C\delta$	47.92		$^{1}Q\beta$	3.75
	$^{1}H\gamma_3$	1.76	Ala4	$^{1}H_N$	8.25		^{15}N	116.9
	$^{13}C\alpha$	61.2		$^{1}H\alpha$	4.23		$^{13}C\alpha$	55.3
	$^{13}C\beta$	27.0		$^{1}Q\beta$	1.32		$^{13}C\beta$	61.3
	$^{13}C\gamma$	24.3		^{15}N	125.6	Ala7	$^{1}H_N$	8.25
	$^{13}C\delta$	47.2		$^{13}C\alpha$	49.8		$^{1}H\alpha$	4.54
Glu2	$^{1}H_N$	8.30		$^{13}C\beta$	16.4		$^{1}Q\beta$	1.27
	$^{1}H\alpha$	4.62	Lys5	$^{1}H_N$	8.25		^{15}N	127.2
	$^{1}H\beta_2$	2.03		$^{1}H\alpha$	4.25		$^{13}C\alpha$	47.8
	$^{1}H\beta_3$	1.83		$^{1}H\beta_2$	1.74		$^{13}C\beta$	15.3
	$^{1}Q\gamma$[a]	2.45		$^{1}H\beta_3$	1.67	Pro8	$^{1}H\alpha$	4.33
	^{15}N	120.4		$^{1}Q\gamma$	1.37		$^{1}Q\beta$	2.19
	$^{13}C\alpha$	50.8		$^{1}Q\delta$	1.60		$^{1}H\gamma_2$	1.90
	$^{13}C\beta$	25.7		$^{1}Q\varepsilon$	2.92		$^{1}H\gamma_3$	1.81
Pro3	$^{1}H\alpha$	4.33		^{1}Qz	7.46		$^{1}H\delta_2$	3.73
	$^{1}Q\beta$	2.23		^{15}N	120.6		$^{1}H\delta_3$	3.56
	$^{1}H\delta_2$	3.72		$^{13}C\alpha$	53.6		$^{13}C\alpha$	60.0
	$^{1}H\delta_3$	3.62		$^{13}C\beta$	30.2		$^{13}C\beta$	29.9

[a] Q= Equivalent protons.

Table S2. (Continuation) Resonance assignments for $H2B_{1-31}$ at pH 2, 298 K (ppm related to TMS).

Residue	Atom	δ/ppm	Residue	Atom	δ/ppm	Residue	Atom	δ/ppm
Pro8	$^{13}C\gamma$	24.6	Lys11	$^{1}Q\varepsilon$	2.92	Gly13	^{15}N	110.6
	$^{13}C\delta$	47.8		^{1}Qz	7.5		$^{13}C\alpha$	42.4
Ala9	$^{1}H_N$	8.32		^{15}N	123.3	Ser14	$^{1}H_N$	8.14
	$^{1}H\alpha$	4.51		$^{13}C\alpha$	53.6		$^{1}H\alpha$	4.38
	$^{1}Q\beta$[a]	1.28		$^{13}C\beta$	30.3		$^{1}Q\beta$	3.79
	^{15}N	125.8		$^{13}C\gamma$	22.0		^{15}N	115.51
	$^{13}C\alpha$	47.6		$^{13}C\delta$	28.2		$^{13}C\alpha$	55.51
	$^{13}C\beta$	15.4		$^{13}C\varepsilon$	39.4		$^{13}C\beta$	61.38
Pro10	$^{1}H\alpha$	4.33	Lys12	$^{1}H_N$	8.29	Lys15	$^{1}H_N$	8.35
	$^{1}Q\beta$	2.22		$^{1}H\alpha$	4.24		$^{1}H\alpha$	4.23
	$^{1}H\gamma_2$	1.96		$^{1}H\beta_2$	1.75		$^{1}H\beta_2$	1.74
	$^{1}H\gamma_3$	1.82		$^{1}H\beta_3$	1.67		$^{1}H\beta_3$	1.67
	$^{1}H\delta_2$	3.73		$^{1}Q\gamma$	1.39		$^{1}Q\gamma$	1.36
	$^{1}H\delta_3$	3.55		$^{1}Q\delta$	1.60		$^{1}Q\delta$	1.59
	$^{13}C\alpha$	60.1		$^{1}Q\varepsilon$	2.91		$^{1}Q\varepsilon$	2.91
	$^{13}C\beta$	29.3		^{1}Qz	7.46		^{1}Qz	7.48
	$^{13}C\gamma$	24.6		^{15}N	123.1		^{15}N	122.9
	$^{13}C\delta$	48.6		$^{13}C\alpha$	53.6		$^{13}C\alpha$	53.6
Lys11	$^{1}H_N$	8.37		$^{13}C\beta$	30.4		$^{13}C\beta$	30.4
	$^{1}H\alpha$	4.25		$^{13}C\gamma$	21.9		$^{13}C\gamma$	22.0
	$^{1}H\beta_2$	1.75		$^{13}C\delta$	26.4		$^{13}C\delta$	26.4
	$^{1}H\beta_3$	1.68		$^{13}C\varepsilon$	39.4		$^{13}C\varepsilon$	39.4
	$^{1}Q\gamma$	1.35	Gly13	$^{1}H_N$	8.42	Lys16	$^{1}H_N$	8.30
	$^{1}Q\delta$	1.55		$^{1}Q\alpha$	3.92		$^{1}H\alpha$	4.22

[a] Q= Equivalent protons.

Table S2. (Continuation) Resonance assignments for $H2B_{1-31}$ at pH 2, 298 K (ppm related to TMS).

Residue	Atom	δ/ppm	Residue	Atom	δ/ppm	Residue	Atom	δ/ppm
Lys16	$^{1}H\beta_2$	1.76	Val18	$^{13}C\alpha$	59.5	Lys20	$^{13}C\delta$	26.3
	$^{1}H\beta_3$	1.69		$^{13}C\beta$	30.1		$^{13}C\varepsilon$	39.4
	$^{1}Q\gamma$[a]	1.38		$^{13}C\gamma_1$	17.7	Ala21	$^{1}H_N$	8.23
	$^{1}Q\delta$	1.60		$^{13}C\gamma_2$	18.4		$^{1}H\alpha$	4.20
	$^{1}Q\varepsilon$	2.92	Thr19	$^{1}H_N$	8.20		$^{1}Q\beta$	1.29
	^{1}Qz	7.46		$^{1}H\alpha$	4.26		^{15}N	125.4
	^{15}N	124.2		$^{1}H\beta$	4.10		$^{13}C\alpha$	49.8
	$^{13}C\alpha$	53.5		$^{1}Q\gamma_2$	1.13		$^{13}C\beta$	16.4
	$^{13}C\beta$	30.3		^{15}N	119.3	Gln22	$^{1}H_N$	8.28
	$^{13}C\gamma$	22.0		$^{13}C\alpha$	59.0		$^{1}H\alpha$	4.24
	$^{13}C\delta$	26.2		$^{13}C\beta$	67.2		$^{1}H\beta_2$	2.00
	$^{13}C\varepsilon$	39.5		$^{13}C\gamma_2$	18.8		$^{1}H\beta_3$	1.89
Ala17	$^{1}H_N$	8.28	Lys20	$^{1}H_N$	8.23		$^{1}Q\gamma$	2.32
	$^{1}H\alpha$	4.27		$^{1}H\alpha$	4.21		$^{1}H\varepsilon_{21}$	7.59
	$^{1}Q\beta$	1.29		$^{1}H\beta_2$	1.73		$^{1}H\varepsilon_{22}$	7.05
	^{15}N	126.3		$^{1}H\beta_3$	1.67		^{14}N	120.3
	$^{13}C\alpha$	49.5		$^{1}Q\gamma$	1.38		$^{15}N\varepsilon_2$	108.8
	$^{13}C\beta$	16.5		$^{1}Q\delta$	1.61		$^{13}C\alpha$	53.1
Val18	$^{1}H_N$	8.16		$^{1}Q\varepsilon$	2.92		$^{13}C\beta$	27.0
	$^{1}H\alpha$	4.10		^{1}Qz	7.47		$^{13}C\gamma$	31.1
	$^{1}H\beta$	2.00		^{15}N	122.8	Lys23	$^{1}H_N$	8.33
	$^{1}Q\gamma_1$	0.88		$^{13}C\alpha$	53.6		$^{1}H\alpha$	4.21
	$^{1}Q\gamma_2$	0.86		$^{13}C\beta$	30.5		$^{1}H\beta_2$	1.75
	^{15}N	120.4		$^{13}C\gamma$	22.0		$^{1}H\beta_3$	1.67

[a] Q= Equivalent protons.

Table S2. (Continuation) Resonance assignments for $H2B_{1-31}$ at pH 2, 298 K (ppm related to TMS).

Residue	Atom	δ/ppm	Residue	Atom	δ/ppm	Residue	Atom	δ/ppm
Lys23	^{1}Qγ[a]	1.32	Asp25	$^{1}H_N$	8.42	Lys27	^{13}Cγ	21.981
	^{1}Qδ	1.61		^{1}Hα	4.64		^{13}Cδ	26.284
	^{1}Qε	2.93		$^{1}Hβ_2$	2.84		^{13}Cε	39.304
	^{1}Qz	7.47		$^{1}Hβ_3$	2.78	Lys28	$^{1}H_N$	8.237
	^{15}N	124.4		^{15}N	120.5		^{1}Hα	4.211
	^{13}Cα	53.6		^{13}Cα	50.4		^{1}Qβ	1.728
	^{13}Cβ	30.3		^{13}Cβ	36.0		$^{1}Hγ_2$	1.366
	^{13}Cγ	22.0	Asp25	$^{1}H_N$	8.31		$^{1}Hγ_3$	1.309
	^{13}Cδ	26.4		$^{1}Hα_1$	3.79		^{1}Qδ	1.624
	^{13}Cε	39.3		$^{1}Hα_2$	3.94		^{1}Qε	2.921
Lys24	$^{1}H_N$	8.35		^{15}N	109.537		^{1}Qz	7.459
	^{1}Hα	4.22		^{13}Cα	42.633		^{15}N	123.296
	$^{1}Hβ_2$	1.75	Lys27	$^{1}H_N$	8.08	Lys28	^{13}Cα	53.738
	$^{1}Hβ_3$	1.67		^{1}Hα	4.233		^{13}Cβ	30.33
	^{1}Qγ	1.34		$^{1}Hβ_2$	1.732		^{13}Cγ	22.067
	^{1}Qδ	1.60		$^{1}Hβ_3$	1.671		^{13}Cδ	26.242
	^{1}Qε	2.91		$^{1}Hγ_2$	1.37		^{13}Cε	39.207
	^{1}Qz	7.49		$^{1}Hγ_3$	1.32	Arg29	$^{1}H_N$	8.349
	^{15}N	123.6		^{1}Qδ	1.6		^{1}Hα	4.207
	^{13}Cα	53.6		^{1}Qε	2.91		$^{1}Hβ_2$	1.69
	^{13}Cβ	30.4		^{1}Qz	7.467		$^{1}Hβ_3$	1.763
	^{13}Cγ	22.0		^{15}N	120.73		^{1}Qγ	1.588
	^{13}Cδ	26.4		^{13}Cα	53.668		^{1}Qδ	3.134
	^{13}Cε	39.4		^{13}Cβ	30.301		^{1}Hε	7.124

[a] Q= Equivalent protons.

Table S2. (Continuation) Resonance assignments for $H2B_{1-31}$ at pH 2, 298 K (ppm related to TMS).

Residue	Atom	δ/ppm	Residue	Atom	δ/ppm	Residue	Atom	δ/ppm
Arg29	$^{1}H_{H21}$	7.46	Lys30	$^{1}Q\delta$[a]	1.601	Arg31	$^{1}H\beta_{3}$	1.67
	$^{1}H_{H22}$	6.809		$^{1}Q\varepsilon$	2.918		$^{1}Q\gamma$	1.56
	^{15}N	121.988		^{1}Qz	7.462		$^{1}Q\delta$	3.122
	$^{15}N_{H2}$	111.85		^{15}N	123.279		$^{1}H\varepsilon$	7.108
	$^{13}C\alpha$	53.461		$^{13}C\alpha$	53.434		$^{1}H_{H21}$	7.462
	$^{13}C\beta$	28.155		$^{13}C\beta$	30.296		$^{1}H_{H22}$	6.799
	$^{13}C\gamma$	24.36		$^{13}C\gamma$	21.976		^{15}N	121.152
	$^{13}C\delta$	40.583		$^{13}C\delta$	26.357		$^{15}N_{H2}$	112.363
Lys30	$^{1}H_{N}$	8.323		$^{13}C\varepsilon$	39.263		$^{13}C\alpha$	53.488
	$^{1}H\alpha$	4.193	Arg31	$^{1}H_{N}$	8.295		$^{13}C\beta$	28.293
	$^{1}H\beta_{2}$	1.741		$^{1}H\alpha$	4.248		$^{13}C\gamma$	40.687
	$^{1}H\beta_{3}$	1.67		$^{1}H\beta_{2}$	1.742		$^{13}C\delta$	24.354
	$^{1}Q\gamma$	1.327						

[a] Q= Equivalent protons.

Table S3. Resonance assignments for $H2B_{1-31}$ (free and Ni^{2+}-bound state) and chemical shifts differences at pH 10.1, 298K (ppm related to TMS).

Residue	Atom	Free/ppm	Ni^{2+}-bound/ppm	Δδ/ppm	Residue	Atom	Free/ppm	Ni^{2+}-bound/ppm	Δδ/ppm
Pro1	$^{1}H\alpha$	4.504	4.510	0.01	Pro3	$^{1}H\gamma_2$	3.774	3.770	0.00
	$^{1}H\beta_2$	2.304	2.307	0.00		$^{1}H\gamma_3$	3.635	3.640	0.01
	$^{1}H\beta_3$	1.999	2.000	0.00		$^{13}C\alpha$	60.465	60.469	0.00
	$^{1}H\delta_2$	1.876	1.880	0.00		$^{13}C\beta$	29.260	29.319	0.06
	$^{1}H\delta_3$	1.787	1.800	0.01		$^{13}C\delta$	47.975	48.096	0.12
	$^{1}H\gamma_2$	3.477	3.478	0.00		$^{13}C\gamma$	24.613	24.664	0.05
	$^{1}H\gamma_3$	3.434	3.434	0.00	Ala4	$^{1}H\alpha$	4.229	4.224	0.00
	$^{13}C\alpha$	61.186	61.210	0.02		$^{1}Q\beta$	1.327	1.329	0.00
	$^{13}C\beta$	26.886	-	-		$^{13}C\alpha$	49.733	49.758	0.03
	$^{13}C\gamma$	24.196	24.215	0.02		$^{13}C\beta$	16.207	16.290	0.08
	$^{13}C\delta$	46.706	46.651	-0.05	Lys5	$^{1}H\alpha$	4.264	4.271	0.01
Glu2	$^{1}H\alpha$	4.513	4.509	0.00		$^{1}H\beta_2$	1.787	1.784	0.00
	$^{1}H\beta_2$	1.947	1.963	0.02		$^{1}H\beta_3$	1.700	1.707	0.01
	$^{1}H\beta_3$	1.842	1.851	0.01		$^{1}Q\gamma$	1.573	1.378	-0.20
	$^{1}Q\gamma$[a]	2.240	2.244	0.00		$^{1}Q\delta$	1.378	1.584	0.21
	$^{13}C\alpha$	51.761	51.598	-0.16		$^{1}Q\varepsilon$	2.841	2.859	0.02
	$^{13}C\beta$	27.085	27.058	-0.03		$^{13}C\alpha$	53.442	53.466	0.02
	$^{13}C\gamma$	33.342	33.278	-0.06		$^{13}C\beta$	30.402	27.034	-3.37
Pro3	$^{1}H\alpha$	4.326	4.326	0.00		$^{13}C\gamma$	22.126	30.334	8.21
	$^{1}Q\beta$	2.237	2.245	0.01		$^{13}C\delta$	27.234	22.017	-5.22
	$^{1}H\delta_2$	1.959	1.960	0.00		$^{13}C\varepsilon$	39.394	39.440	0.05
	$^{1}H\delta_3$	1.846	1.851	0.00	Ser6	$^{1}H\alpha$	4.376	4.371	0.00

[a] Q= Equivalent protons.

Table S3. (Continuation) Resonance assignments for $H2B_{1-31}$ (free and Ni^{2+}-bound state) and chemical shifts differences at pH 10.1, 298K (ppm related to TMS).

Residue	Atom	Free/ppm	Ni^{2+}-bound/ppm	Δδ/ppm	Residue	Atom	Free/ppm	Ni^{2+}-bound/ppm	Δδ/ppm
Ser6	$^{1}H\beta_2$	3.768	3.765	0.00	Pro10	$^{1}H\alpha$	4.350	4.357	0.01
	$^{1}H\beta_3$	3.825	-	-		$^{1}Q\beta$	2.218	2.220	0.00
	$^{13}C\alpha$	55.182	55.229	0.05		$^{1}H\gamma_2$	1.960	1.966	0.01
	$^{13}C\beta$	61.153	61.042	-0.11		$^{1}H\gamma_3$	1.812	1.816	0.00
Ala7	$^{1}H\alpha$	4.553	4.563	0.01		HD2	3.747	3.744	0.00
	$^{1}Q\beta$	1.290	1.306	0.02		HD3	3.584	3.584	0.00
	$^{13}C\alpha$	47.722	47.688	-0.03		$^{13}C\alpha$	60.135	60.144	0.01
	$^{13}C\beta$	15.327	15.310	-0.02		$^{13}C\beta$	29.903	29.233	-0.67
Pro8	$^{1}H\alpha$	4.342	4.348	0.01		$^{13}C\gamma$	24.733	24.518	-0.22
	$^{1}Q\beta$[a]	2.215	2.207	-0.01		$^{13}C\delta$	48.752	47.683	-1.07
	$^{1}H\gamma_2$	1.958	1.955	0.00	Lys11	$^{1}H\alpha$	4.265	4.272	0.01
	$^{1}H\gamma_3$	-	1.828	-0.13		$^{1}H\beta_2$	1.766	1.777	0.01
	$^{1}H\delta_2$	3.727	3.729	0.00		$^{1}H\beta_3$	1.686	1.696	0.01
Pro8	$^{1}H\delta_3$	3.572	3.570	0.00		$^{1}Q\gamma$	1.310	1.311	0.00
	$^{13}C\alpha$	59.849	59.798	-0.05		$^{1}Q\delta$	1.382	1.385	0.00
	$^{13}C\beta$	29.870	29.313	-0.56		$^{1}Q\varepsilon$	2.757	2.815	0.06
	$^{13}C\gamma$	24.642	24.476	-0.17		$^{13}C\alpha$	53.607	53.492	-0.12
	$^{13}C\delta$	47.690	0.000	0.00		$^{13}C\beta$	30.390	30.312	-0.08
Ala9	$^{1}H\alpha$	4.508	4.524	0.02		$^{13}C\gamma$	22.190	22.210	0.02
	$^{1}Q\beta$	1.299	1.300	0.00		$^{13}C\delta$	29.094	29.104	0.01
	$^{13}C\alpha$	47.527	47.584	0.06		$^{13}C\varepsilon$	39.683	39.392	-0.29
	$^{13}C\beta$	15.330	16.422	1.09	Lsy12	$^{1}H\alpha$	4.229	4.227	0.00

[a] Q= Equivalent protons.

Table S3. (Continuation) Resonance assignments for $H2B_{1-31}$ (free and Ni^{2+}-bound state) and chemical shifts differences at pH 10.1, 298K (ppm related to TMS).

Residue	Atom	Free/ppm	Ni^{2+}-bound/ppm	Δδ/ppm	Residue	Atom	Free/ppm	Ni^{2+}-bound/ppm	Δδ/ppm
Lsy12	$^{1}H\beta_2$	1.756	1.734	-0.02	Lys15	$^{1}Q\varepsilon$	2.760	2.931	0.17
	$^{1}H\beta_3$	1.678	-	-		$^{13}C\alpha$	53.684	54.130	0.45
	$^{1}H\gamma_2$	1.383	1.316	-0.07		$^{13}C\beta$	30.378	30.378	0.00
	$^{1}H\gamma_3$	1.333	-	-		$^{13}C\gamma$	22.361	22.361	0.00
	$^{1}Q\delta$[a]	1.493	1.525	0.03		$^{13}C\delta$	29.100	29.100	0.00
	$^{1}Q\varepsilon$	2.744	2.929	0.19		$^{13}C\varepsilon$	40.839	40.839	1.27
	$^{13}C\alpha$	53.581	53.862	0.28	Lys16	$^{1}H\alpha$	4.208	4.166	-0.04
	$^{13}C\beta$	30.293	30.355	0.06		$^{1}H\beta_2$	1.742	2.032	0.29
	$^{13}C\gamma$	22.235	22.276	0.04		$^{1}H\beta_3$	1.695	-	0.34
	$^{13}C\delta$	28.406	27.964	-0.44		$^{1}H\gamma_2$	1.380	1.707	0.33
	$^{13}C\varepsilon$	39.618	40.922	1.30		$^{1}H\gamma_3$	1.318	1.629	0.31
Gly13	$^{1}Q\alpha$	3.911	3.875	-0.04		$^{1}Q\delta$	1.524	1.800	0.28
	$^{13}C\alpha$	42.188	42.672	0.48		$^{1}Q\varepsilon$	2.785	3.043	0.26
Ser14	$^{1}H\alpha$	4.396	3.958	-0.44		$^{13}C\alpha$	53.907	53.461	-0.45
	$^{1}Q\beta$	3.799	3.563	-0.24		$^{13}C\beta$	30.259	31.462	1.20
	$^{13}C\alpha$	55.530	-	-		$^{13}C\gamma$	22.248	22.060	-0.19
	$^{13}C\beta$	61.125	-	-		$^{13}C\delta$	28.241	-	-
Lys15	$^{1}H\alpha$	4.249	4.178	-0.07		$^{13}C\varepsilon$	39.588	41.800	2.21
	$^{1}H\beta_2$	1.764	-	2.41	Ala17	$^{1}H\alpha$	4.267	4.420	0.15
	$^{1}H\beta_3$	1.691	1.713	0.02		$^{1}Q\beta$	1.310	0.908	-0.40
	$^{1}Q\gamma$	1.371	1.283	-0.09		$^{13}C\alpha$	49.611	50.911	1.30
	$^{1}Q\delta$	1.515	1.391	-0.12		$^{13}C\beta$	16.379	-	-

[a] Q= Equivalent protons.

Table S3. (Continuation) Resonance assignments for $H2B_{1-31}$ (free and Ni^{2+}-bound state) and chemical shifts differences at pH 10.1, 298K (ppm related to TMS).

Residue	Atom	Free/ppm	Ni^{2+}-bound/ppm	Δδ/ppm	Residue	Atom	Free/ppm	Ni^{2+}-bound/ppm	Δδ/ppm
Val18	$^{1}H\alpha$	4.101	3.004	-1.10	Lys20	$^{13}C\beta$	30.330	30.514	0.18
	$^{1}H\beta$	2.026	1.304	-0.72		$^{13}C\gamma$	22.133	-	-
	$^{1}Q\gamma_2$[a]	0.893	1.024	0.13		$^{13}C\delta$	27.989	-	-
	$^{1}Q\gamma_3$	0.880		0.14		$^{13}C\varepsilon$	39.529	-	-
	$^{13}C\alpha$	59.532	53.743	-5.79	Ala21	$^{1}H\alpha$	4.209	3.575	-0.63
	$^{13}C\beta$	30.060	29.074	-0.99		$^{1}Q\beta$	1.291	1.391	0.10
	$^{13}C\gamma_1$	17.725	18.505	0.78		$^{13}C\alpha$	49.883	-	-
	$^{13}C\gamma_2$	18.387		0.12		$^{13}C\beta$	16.483	16.327	-0.16
Thr19	$^{1}H\alpha$	4.277	5.076	0.80	Gln22	$^{1}H\alpha$	4.234	3.045	-1.19
	$^{1}H\beta$	4.136	2.935	-1.20		$^{1}H\beta_2$	2.023	1.815	-0.21
	$^{1}Q\gamma_2$	1.148	1.380	0.23		$^{1}H\beta_3$	1.938	-	-0.12
	$^{13}C\alpha$	58.977	-	-		$^{1}Q\gamma$	2.323	2.239	-0.08
	$^{13}C\beta$	67.092	61.066	-6.03	Gln22	$^{13}C\alpha$	53.106	55.650	2.54
	$^{13}C\gamma_2$	18.786	16.359	-2.43		$^{13}C\beta$	26.823	29.247	2.42
Lys20	$^{1}H\alpha$	4.213	3.957	-0.26		$^{13}C\gamma$	30.998	33.317	2.32
	$^{1}H\beta_2$	1.757	1.738	-0.02	Lys23	$^{1}H\alpha$	4.209	3.626	-0.58
	$^{1}H\beta_3$	1.694	1.808	0.11		$^{1}H\beta_2$	1.735	1.892	0.16
	$^{1}Q\gamma$	1.366	2.058	0.69		$^{1}H\beta_3$	1.694	-	0.20
	$^{1}Q\delta$	1.538	-	-		$^{1}Q\gamma$	1.322	1.740	0.42
	$^{1}H\varepsilon_2$	2.770	3.446	0.68		$^{1}Q\delta$	1.512	1.510	0.00
	$^{1}H\varepsilon_3$	-	3.239	0.47		$^{1}Q\varepsilon$	2.740	3.150	0.41
	$^{13}C\alpha$	53.758	64.993	11.24		$^{13}C\alpha$	53.828	58.289	4.46

[a] Q= Equivalent protons.

Table S3. (Continuation) Resonance assignments for $H2B_{1-31}$ (free and Ni^{2+}-bound state) and chemical shifts differences at pH 10.1, 298K (ppm related to TMS).

Residue	Atom	Free/ppm	Ni^{2+}-bound/ppm	Δδ/ppm	Residue	Atom	Free/ppm	Ni^{2+}-bound/ppm	Δδ/ppm
Lys23	$^{13}C\beta$	30.297	-	-	Lys27	$^{1}H\alpha$	4.218	4.204	-0.01
	$^{13}C\gamma$	22.210	22.128	-0.08		$^{1}H\beta_2$	1.753	-	2.45
	$^{13}C\delta$	28.304	27.853	-0.45		$^{1}H\beta_3$	1.686	1.700	0.01
	$^{13}C\varepsilon$	39.500	40.433	0.93		$^{1}Q\gamma$	1.315	1.384	0.07
Lys24	$^{1}H\alpha$	4.235	3.562	-0.06		$^{1}Q\delta$	1.512	1.321	-0.19
	$^{1}H\beta_2$	1.755	2.086	0.33		$^{1}Q\varepsilon$	2.754	2.922	0.17
	$^{1}H\beta_3$	1.709	-	0.38		$^{13}C\alpha$	53.842	53.438	-0.40
	$^{1}Q\gamma$[a]	1.377	1.545	0.17		$^{13}C\beta$	30.428	30.355	-0.07
	$^{1}Q\delta$	1.507	1.545	0.04		$^{13}C\gamma$	22.266	22.129	-0.14
	$^{1}Q\varepsilon$	2.747	2.794	0.05		$^{13}C\delta$	28.381	29.013	0.63
	$^{13}C\alpha$	53.731	62.060	8.33		$^{13}C\varepsilon$	39.581	40.910	1.33
	$^{13}C\beta$	30.348	26.808	-3.54	Lys28	$^{1}H\alpha$	4.194	4.194	0.00
	$^{13}C\gamma$	22.046	22.110	0.06		$^{1}Q\beta$	1.712	1.747	0.04
	$^{13}C\delta$	28.443	27.902	-0.54		$^{1}Q\gamma$	1.375	1.375	0.00
	$^{13}C\varepsilon$	39.559	39.486	-0.07		$^{1}Q\delta$	1.519	1.560	0.04
Asp25	$^{1}H\alpha$	4.512	3.589	-0.92		$^{1}Q\varepsilon$	2.753	2.816	0.06
	$^{1}Q\beta$	2.627	3.190	0.56		$^{13}C\alpha$	53.904	53.983	0.08
	$^{13}C\alpha$	51.632	-	0.00		$^{13}C\beta$	30.298	30.331	0.03
	$^{13}C\beta$	38.557	-	0.00		$^{13}C\gamma$	22.200	22.118	-0.08
Gly26	$^{1}H\alpha_1$	3.892	2.985	-0.91		$^{13}C\delta$	28.425	27.446	-0.98
	$^{1}H\alpha_2$	3.841	2.895	-0.95		$^{13}C\varepsilon$	39.617	39.404	-0.21
	$^{13}C\alpha$	42.788	-	-	Arg29	$^{1}H\alpha$	4.224	4.225	0.00

[a] Q= Equivalent protons.

Table S3. (Continuation) Resonance assignments for $H2B_{1-31}$ (free and Ni^{2+}-bound state) and chemical shifts differences at pH 10.1, 298K (ppm related to TMS).

Residue	Atom	Free/ppm	Ni^{2+}-bound/ppm	Δδ/ppm	Residue	Atom	Free/ppm	Ni^{2+}-bound/ppm	Δδ/ppm
Arg29	$^{1}H\beta_2$	1.797	1.798	0.00		$^{13}C\alpha$	53.558	53.535	-0.02
	$^{1}H\beta_3$	1.708	1.713	0.01		$^{13}C\beta$	30.223	30.366	0.14
	$^{1}Q\gamma$[a]	1.614	1.592	-0.02		$^{13}C\gamma$	22.137	22.120	-0.02
	$^{1}Q\delta$	3.159	3.155	0.00		$^{13}C\delta$	28.485	27.627	-0.86
	$^{13}C\alpha$	53.783	53.798	0.02		$^{13}C\varepsilon$	39.007	39.474	0.47
	$^{13}C\beta$	28.082	28.140	0.06	Arg31	$^{1}H\alpha$	4.241	4.247	0.01
	$^{13}C\gamma$	24.471	24.404	-0.07		$^{1}H\beta_2$	1.778	1.778	0.00
	$^{13}C\delta$	40.437	40.489	0.05		$^{1}H\beta_3$	1.688	1.686	0.00
Lys30	$^{1}H\alpha$	4.203	4.204	0.00		$^{1}Q\gamma$	1.556	1.555	0.00
	$^{1}H\beta_2$	1.752	1.772	0.02		$^{1}Q\delta$	3.137	3.136	0.00
	$^{1}H\beta_3$	1.691	1.718	0.03		$^{13}C\alpha$	53.751	53.726	-0.02
	$^{1}Q\gamma$	1.315	1.358	0.04		$^{13}C\beta$	28.230	28.049	-0.18
	$^{1}Q\delta$	1.508	1.563	0.05		$^{13}C\gamma$	24.386	24.463	0.08
	$^{1}Q\varepsilon$	2.742	2.818	0.08		$^{13}C\delta$	40.599	40.489	-0.11

[a] Q= Equivalent protons.

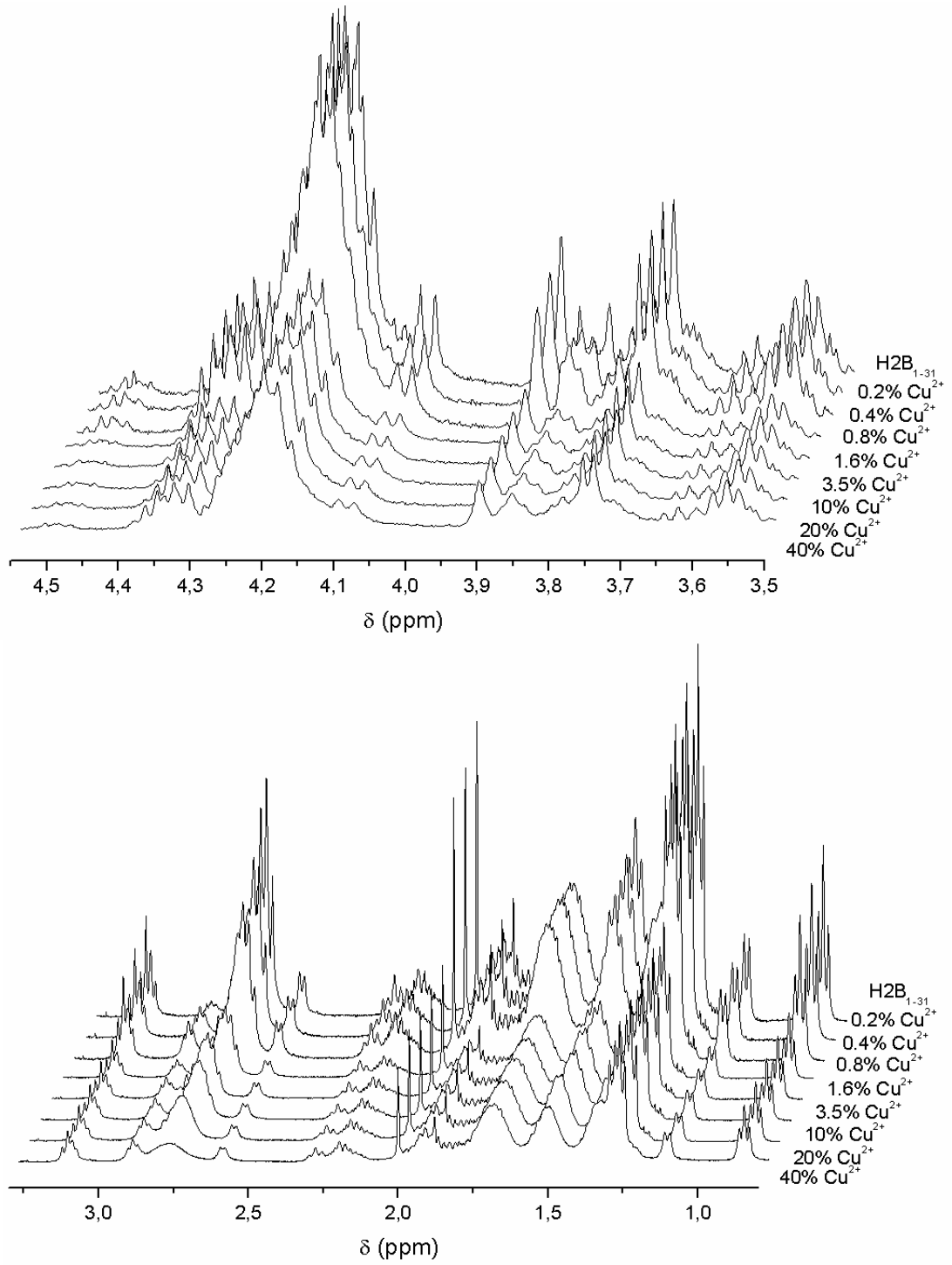

Figure S2 ^{1}H NMR stack plot showing the effect of Cu^{2+} addition to $H2B_{1-31}$ signals (2 mM in 99.9 % D_2O, at pH 10.1, 298 K). $CuCl_2.2H_2O$ was added in aliquots reaching 0.002, 0.004, 0.008, 0.016, 0.035, 0.01, 0.02 and 0.04 mole-equivalents of Cu^{2+}.

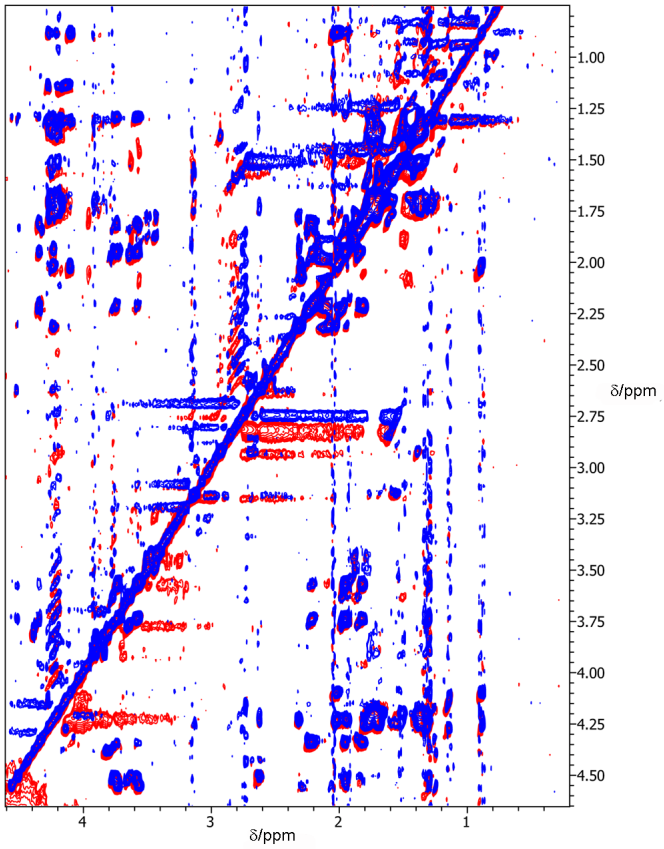

Figure S3. Overlaid aliphatic region of the free $H2B_{1-31}$ (blue) and Ni^{2+}-bound $H2B_{1-31}$ (red) of [^{1}H-^{1}H]-NOESY spectra at a peptide to nickel molar ratio of 1.1:1, at pH 10.1, 298 K.

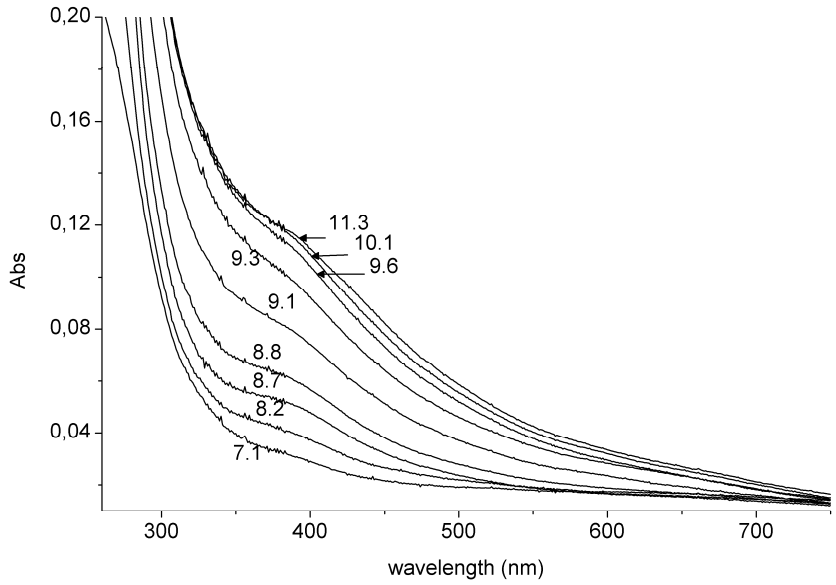

Figure S4. UV/Vis spectra of the Ni^{2+}: $H2B_{1-31}$ system, at various pH values with a molar ratio of 1:1.1 (0.6 mM), at 298 K and I = 0.2 M (KCl).

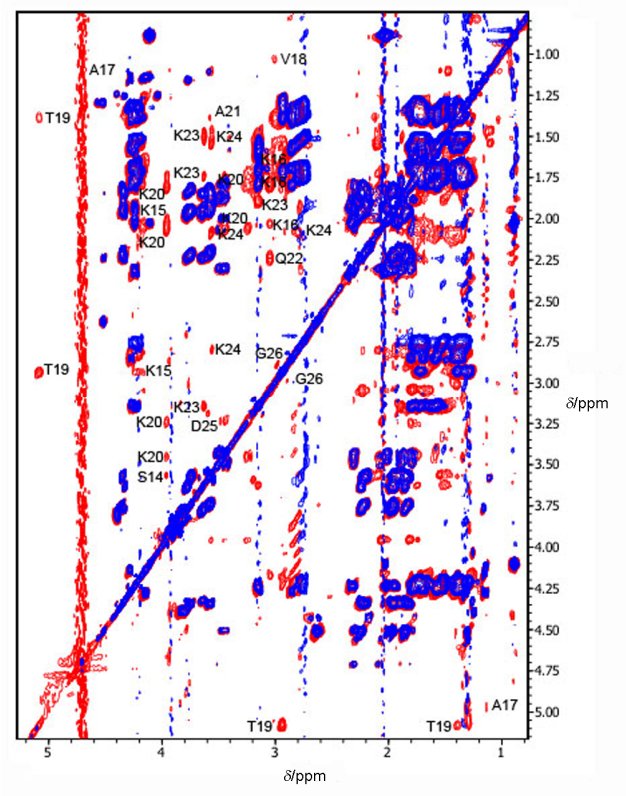

Figure S5. Overlaid aliphatic region of the free $H2B_{1-31}$ (blue) and Ni^{2+}-bound $H2B_{1-31}$ (red) TOCSY spectra at a peptide to nickel molar ratio of 1.1: 1 (pH 10.1, 298 K). New resonances due to Ni^{2+} binding have been labelled.