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Supporting information for article:

Binding of metal ions and water molecules to nucleic acid bases: the influence of water molecule coordination to a metal ion on water– nucleic acid base hydrogen bonds

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Binding of metal ions and water molecules to nucleic bases.
The Influence of Water Molecule Coordination to a Metal Ion on Water-Nucleic Base Hydrogen Bonds

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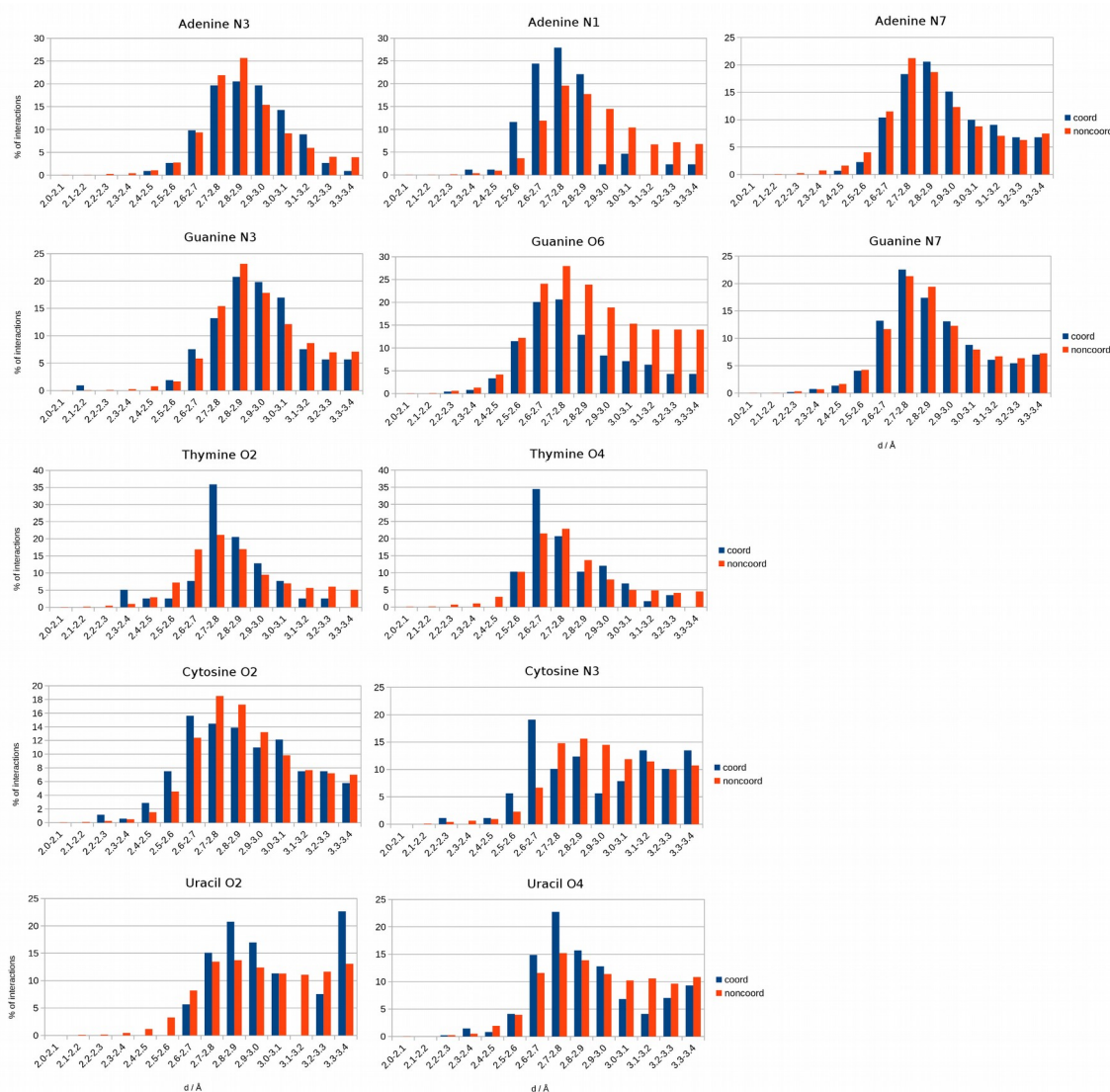
Figure S1. Distance *d* distribution for hydrogen bonds with coordinated and noncoordinated water, separately for different nucleic bases and positions. The positions are defined in Figure 2.

In order to find suitable method for calculations of hydrogen bonds between water molecule and nucleic bases we performed the benchmark study where we compared interaction energies calculated with two methods, B3LYP-D3/def2-TZVP (corrected for BSSE), MP2/def2-QZVP (noncorrected for BSSE) with very accurate CCSD(T)/CBS level (Table S1). The data show that both methods are in very good agreement with CCSD(T)/CBS level. MP2/def2-QZVP are in good agreement with CCSD(T)/CBS values, without BSSE correction, probable because of the error cancelations. For the calculations we used B3LYP-D3/def2-TZVP level, since MP2/def2-QZVP level was very demanding on computer resources, making the calculations on relatively large systems with aqua metal complexes almost impossible.

Table S1. The calculated interaction energies ΔE (kcal/mol) and d distances (Å) (d_{ON} or d_{OO}) between five nucleic bases and noncoordinated water molecules, at the B3LYP-D3/def2-TZVP (corrected for BSSE), MP2/def2-QZVP (noncorrected for BSSE) and CCSD(T)/CBS level. The CCSD(T)/CBS energies were calculated by using Mackie and DiLabio method (Mackie and DiLabio 2011). The different interacting sites are shown in Figure 2.

B3LYP-D3/def2-TZVP									
Base	Base site	ΔE (kcal/mol)	d (Å)	Base site	ΔE (kcal/mol)	d (Å)	Base site	ΔE (kcal/mol)	d (Å)
adenine	N3	-7.25	2.9	N1	-7.96	2.9	N7	-8.69	2.9
guanine	N3	-7.50	2.9	O6	-5.56	3.0	N7	-6.32	3.0
thymine	O2	-4.73	3.0	O4	-5.12	3.0	/	/	/
cytosine	O2	-6.13	2.9	N3	-8.20	2.9	/	/	/
uracil	O2	-4.63	3.0	O4	-4.86	3.0	/	/	/
MP2/def2-QZVP									
adenine	N3	-7.07	2.9	N1	-7.50	2.9	N7	-8.21	2.9
guanine	N3	-7.29	2.9	O6	-5.26	3.0	N7	-6.24	3.0
thymine	O2	-4.63	3.0	O4	-4.89	3.0	/	/	/
cytosine	O2	-6.13	2.9	N3	-7.68	2.9	/	/	/
uracil	O2	-4.58	3.0	O4	-4.62	3.0	/	/	/
CCSD(T)/CBS (Mackie)									
adenine	N3	-6.90	2.9	N1	-7.36	2.9	N7	-7.98	2.9
guanine	N3	-7.01	2.9	O6	-5.40	3.0	N7	-6.08	3.0
thymine	O2	-4.72	3.0	O4	-4.94	3.0	/	/	/
cytosine	O2	-6.90	2.9	N3	-7.53	2.9	/	/	/
uracil	O2	-4.58	3.0	O4	-4.70	3.0	/	/	/

Table S2. The calculated interaction energies ΔE (kcal/mol) and d distances (Å) (d_{ON} or d_{OO}) at the B3LYP-D3/def2-TZVP level between five nucleic bases and water molecules coordinated to Zn^{2+} ion. The different interacting sites are shown in Figure 2.

Coordinated water molecule ($[Zn(H_2O)_6]^{2+}$)									
Base	Base site	ΔE (kcal/mol)	d (Å)	Base site	ΔE (kcal/mol)	d (Å)	Base site	ΔE (kcal/mol)	d (Å)
adenine	N3	-25.19	2.6	N1	-25.61	2.6	N7	-22.78	2.6
guanine	N3	-12.93	2.6	O6	-38.44	2.6	N7	-49.36	2.8
thymine	O2	-24.91	2.6	O4	-27.69	2.6	/	/	/
cytosine	O2	-38.78	2.8	N3	-36.17	2.6	/	/	/
uracil	O2	-23.05	2.6	O4	-27.83	2.6	/	/	/

Table S3. Number of hydrogen bonds between nucleic bases and coordinated water, and percentage of $[M(H_2O)_n]^{x+}$ complexes, with different kinds of metals.

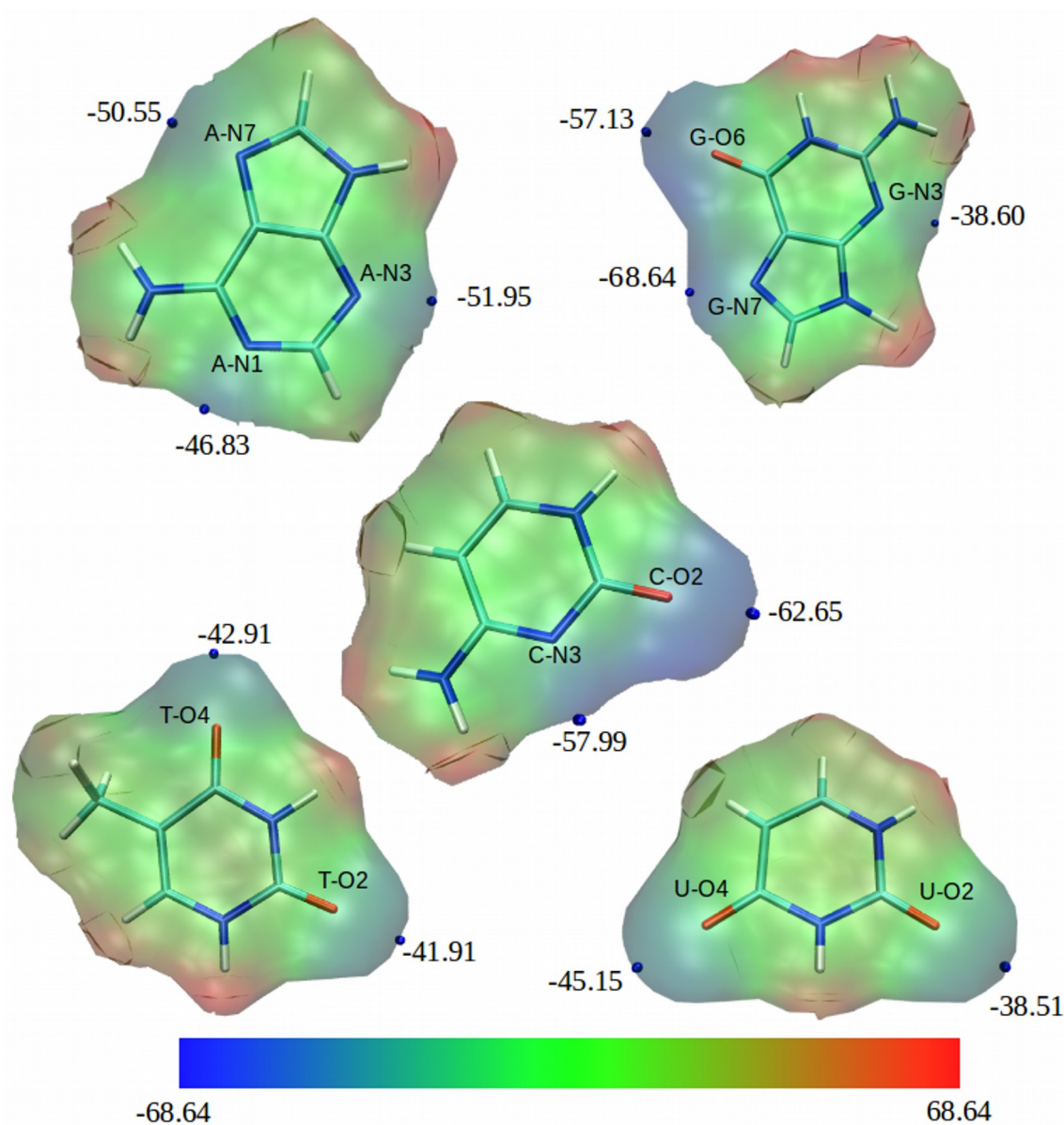| Metal	Number of H bonds with coordinated water	
	All	$[M(H_2O)_n]^{x+}$
Mg^{2+}	2208	1142 (51.7 %)
Sr^{2+}	890	254 (28.5 %)
Na^+	551	94 (17.1 %)
Ca^{2+}	444	242 (54.5 %)
K^+	186	10 (5.4 %)
Mn^{2+}	165	37 (22.4 %)
Ba^{2+}	67	0 (0.0 %)
Zn^{2+}	52	18 (34.6 %)
Co^{2+}	29	9 (31.0 %)
Cu^{2+}	12	2 (16.7 %)
Ni^{2+}	8	0 (0.0 %)
Tl^+	8	5 (62.5 %)
Cd^{2+}	1	0 (0.0 %)
Hg^{2+}	1	0 (0.0 %)
Pt^{2+}	1	0 (0.0 %)

Figure S2. Electrostatic potential maps for the nucleic bases. Model systems taken from 5NYS PDB file and patched with hydrogen atom 1.01 Å far from the nitrogen atoms bound to DNA molecule. Potential was calculated with CUBEGEN implemented in GAUSSIAN, with the grid fineness of 0.1 Å in each dimension. Potentials shown in kcal e^{-1} mol^{-1}. Potential at the marked oxygen and nitrogen sites (blue dots) has been calculated by finding the closest map point to the point in the Van der Waals surface laying in the direction ring centre - oxygen/nitrogen atom. Nucleic bases are labelled with one-letter code. The code for determining the electrostatic potential was written in PYTHON. VMD software was used for visual representation.
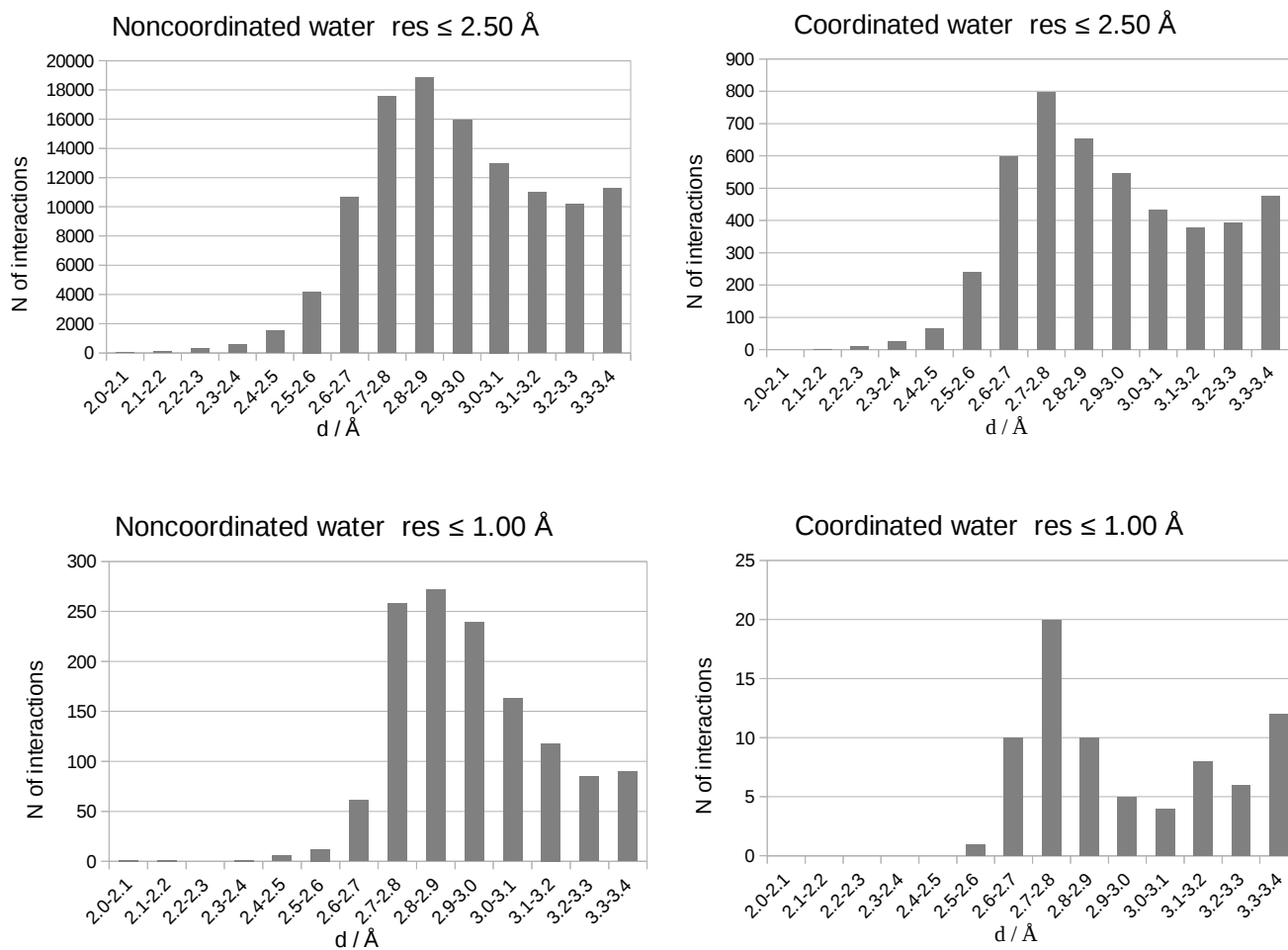
Figure S3. Distribution of the distance between water oxygen and nucleic base oxygen/nitrogen (d_{ON} or d_{OO}) found in PDB structures for noncoordinated and coordinated water. Lower histograms show only high resolution structures ($\leq$ 1.00 Å).