Supplementary Information

The Influence of Water Molecule Coordination to a Metal Ion onto Hydrogen Bonds

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I Calculated interaction energies for P_1/P_2 angle of 90° and 0°

The calculated energies of hydrogen bonds at CCSD(T) limit [s1] are -4.84 and -4.31 kcal/mol for P_1/P_2 angle of 90° and 0° respectively. Because of the larger stability of the hydrogen bonds with P_1/P_2 angle of 90°, we calculated all hydrogen bonds in this work with P_1/P_2 angle of 90°.

II Optimized geometries of the monomers with two DFT methods and MP2 interaction energies

Table S1. Calculated distances (in Å) for monomers optimized with two DFT methods[a]

Model system	B3LYP [s2]			MO6-2x [s3]		
	d_{O-H}	d_{Zn-O}	d_{Zn-Cl}	d_{O-H}	d_{Zn-O}	d_{Zn-Cl}
H_2O	0.965	/	/	0.961	/	/
$[ZnCl_2(H_2O)_4]$	0.964	2.168	2.374	0.962	2.150	2.366
$[ZnCl(H_2O)_5]^+$	0.968	2.253	2.323	0.965	2.179	2.305
$[Zn(H_2O)_6]^{2+}$	0.968	2.131	/	0.967	2.106	/

[a]6-31G** basis set for O, H, Cl and lanl2dz for Zn atom

Table S2. Calculated hydrogen bond energies (in kcal/mol) and hydrogen bond distances (in Å) for four model systems (Figure 4), using MP2 method [s4] and def2-QZVP basis set [s5] for all atoms.

Model System	Rigid monomers			
	MP2//B3LYP[a]		MP2//MO6-2x[b]	
	ΔE	d_{HO}[c]	ΔE	d_{HO}[c]
A	-4.40	1.94	-4.39	1.94
B	-5.42	1.84	-5.41	1.84
C	-12.17	1.73	-12.14	1.74
D	-18.73	1.73	-18.67	1.73

[a] MP2/def2-QZVP interaction energies on B3LYP geometries (Table S1)
[b] MP2/def2-QZVP interaction energies on MO6-2x geometries (Table S1)
[c] d_{HO} is the distance between hydrogen atom and the oxygen atom, Figure 1 (main text).

The geometries of the monomers were optimized with two DFT methods; very often used B3LYP [s2] method and relatively new M06-2X method [s3]. It was shown that M06-2X method accurately predicts the relative energies of water hexamers and noncovalent bonding interactions in other molecular systems [s6].

All bond distances calculated with MO6-2x method are shorter compare to B3LYP distances, however, the difference is very small. The calculated MP2 hydrogen bond energies on MO6-2x and B3LYP monomer geometries are very similar; the MO6-2x geometries have weaker interactions for less than 0.1 kcal/mol (Table S2).

III Curves of calculated interaction energies

The optimized monomer geometries were kept rigid and d_{OO} distance was systematically varied. The calculated interaction energies (ΔE) of OH/O and MLOH/O interaction are plotted in Figure S1, as the function of d_{OO} distance from 2.4 to 4.0 Å .

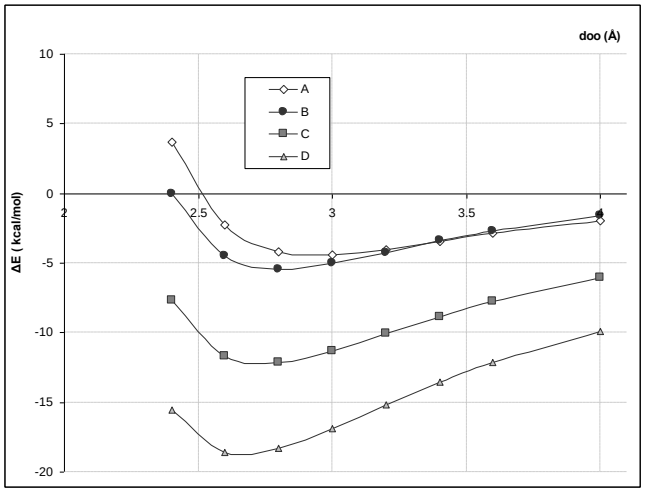
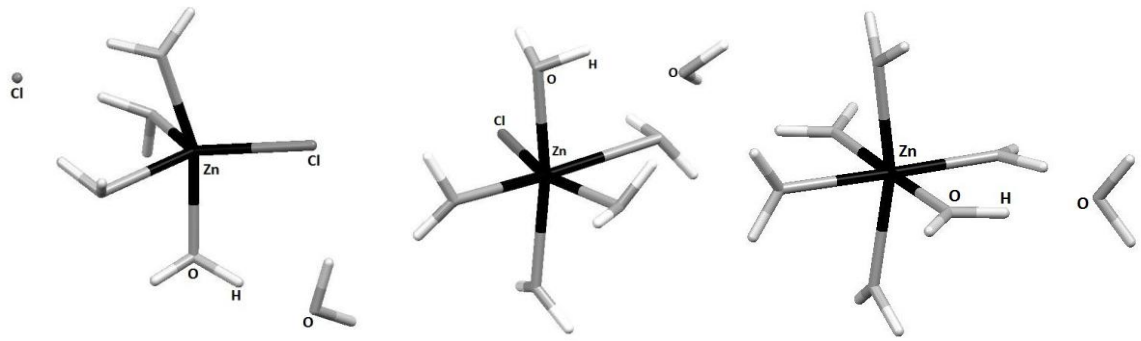


Figure S1. The calculated interaction energies (ΔE) for four different model systems, plotted as a function of d_{OO} distance: A (HOH/HOH), B($[ZnCl_2(H_2O)_4]$/HOH), C ($[ZnCl(H_2O)_5]^+$/HOH) and D ($[Zn(H_2O)_6]^{2+}$/HOH). The model systems A, B, C and D are presented in Figure 4 (main text).

IV Optimized geometries of aqua-complex/water systems

Starting with the most stable aqua-complex/water systems presented in Table 1, complete optimizations were performed, using B3LYP method with lanl2dz basis set [s7] for the zinc atom and 6-31G** basis sets [s8] for the oxygen, chlorine and hydrogen atoms. Results of the optimization are shown in Figure S2 and Table S3.



(a) (b) (c)

Figure S2. Optimized geometries of aqua-complex/water model systems starting with (a) trans-$[ZnCl_2(H_2O)_4]/H_2O$, (b) $[ZnCl(H_2O)_5]^+/H_2O$, and (c) $[Zn(H_2O)_6]^{2+}/H_2O$.

Table S3. Calculated distances (in Å) for model systems

Model system	Rigid monomers			Optimized structures[a]		
	d_{O-H}	d_{Zn-O}	d_{Zn-Cl}	d_{O-H}	d_{Zn-O}	d_{Zn-Cl}
$[ZnCl_2(H_2O)_4]/OH_2$[b]	0.964	2.168	2.374	1.002[b]	2.145	2.304[b]
$[ZnCl(H_2O)_5]^+/OH_2$	0.968	2.253	2.323	0.981	2.165	2.329
$[Zn(H_2O)_6]^{2+}/OH_2$	0.968	2.131	/	0.985	2.107	/

[a] Completely optimized aqua-complex/water model systems (Figure S2)
[b] After optimization complex is pentacoordinated (Figure S2a)

Energies at MP2/def2-QZVP level were calculated using B3LYP optimized geometries. Results of calculations are shown in Table S3. For hexaaqua and pentaaqua complex complete optimization resulted in bifurcated hydrogen bonds of water molecule. The complete optimization of tetraaqua complex resulted in pentacoordianted complex, where one Cl^- ligand is dissociated. The most stable structure (Figure S2c) has interaction energy of -27.61 kcal/mol and two aqua ligands, from hexaaqua complex, that interact with the water molecule.

Table S4. Interaction energies in kcal/mol at MP2/def2-QZVP level on B3LYP optimized geometries of aqua-complex/water systems

Model systems	ΔE
$[ZnCl_2(H_2O)_4]/ OH_2$	/
$[ZnCl(H_2O)_5]^+ / OH_2$	-21.26
$[Zn(H_2O)_6]^{2+}/ OH_2$	-27.61

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