

Supplementary data for the article:

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Supporting Information

Hydrogen Bonding between Metal-Ion Complexes and Noncoordinated Water: Electrostatic Potentials and Interaction Energies

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SUPPLEMENTARY INFORMATION

Potential energy curves of tetrahedral model hydrogen-bonded systems using fixed reactant geometries

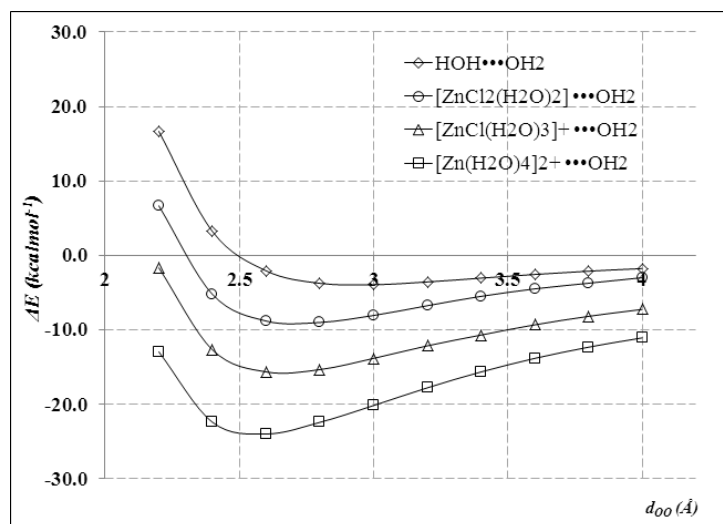


Figure S1. The calculated interaction energies (ΔE) for four different model hydrogen-bonded systems, using fixed reactant geometries. The interaction energies are plotted as a function of d_{O-O} distance: (a) $H_2O \cdots OH_2$, (b) $[ZnCl_2(H_2O)_2] \cdots OH_2$, (c) $[ZnCl(H_2O)_3]^+ \cdots OH_2$, and (d) $[Zn(H_2O)_4]^{2+} \cdots OH_2$. The results are compared with those for the interaction of two non-coordinated water molecules, $HOH \cdots OH_2$. The model systems that were used are shown in **Figure 4**.

Potential energy curves of neutral octahedral model hydrogen-bonded systems using fixed reactant geometries

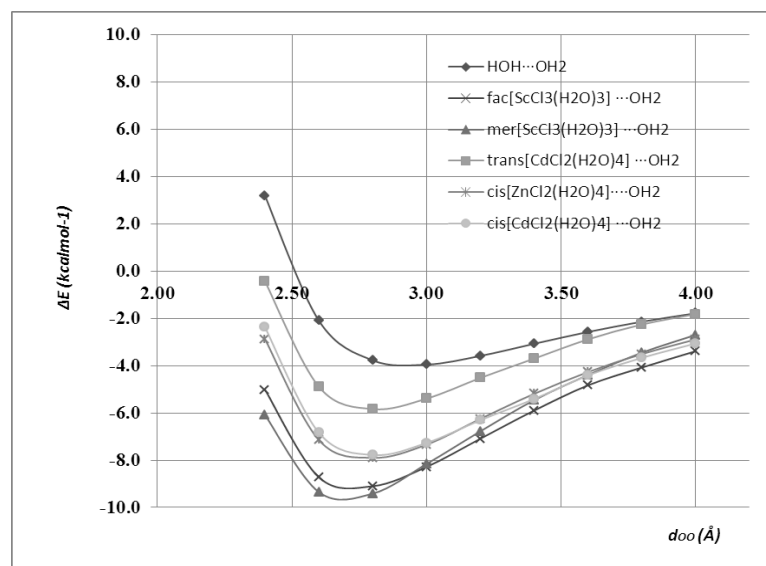


Figure S2. The calculated interaction energies (ΔE) for five different model hydrogen-bonded systems, using fixed reactant geometries. The interaction energies are plotted as a function of the $d_{O...O}$ distance: (a) *fac*-[ScCl₃(H₂O)₃]...OH₂, (b) *mer*-[ScCl₃(H₂O)₃]...OH₂, (c) *trans*-[CdCl₂(H₂O)₄]...OH₂, (d) *cis*-[CdCl₂(H₂O)₄]...OH₂, (e) *cis*-[ZnCl₂(H₂O)₄]...OH₂. The results are compared with those for the interaction of two non-coordinated water molecules HOH...OH₂. The model systems used for (a) – (e) are shown in **Figure 5**.

The distribution of cone-corrected angle α

The preference for linear contact geometries in O–H/O interactions of coordinated water molecule can be observed by the distributions of angle α . To obtain more reliable data, cone correction should be used [1]. Namely, the angle covered by an angular interval $\Delta\alpha$ is smaller for nearly linear angles α than for bent ones and the angular distribution must be weighted by a correction factor of $1/\sin\alpha$ to properly reflect angular preferences. In corrected diagrams larger fractions of the interactions are obtained at larger angles.

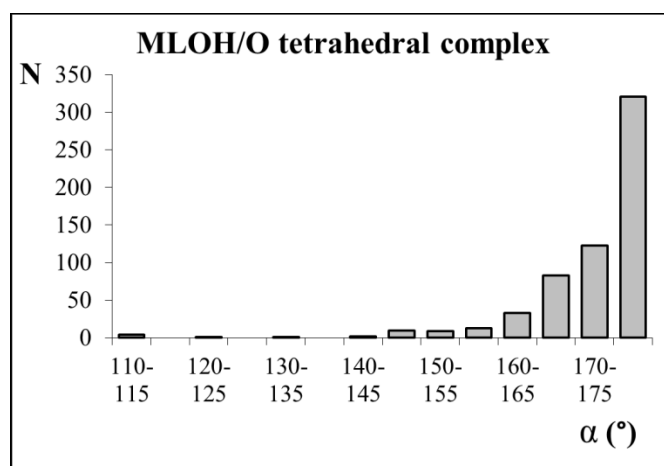


Figure S3. The distribution of cone-corrected angle α (Fig. 3) for tetrahedral complexes.

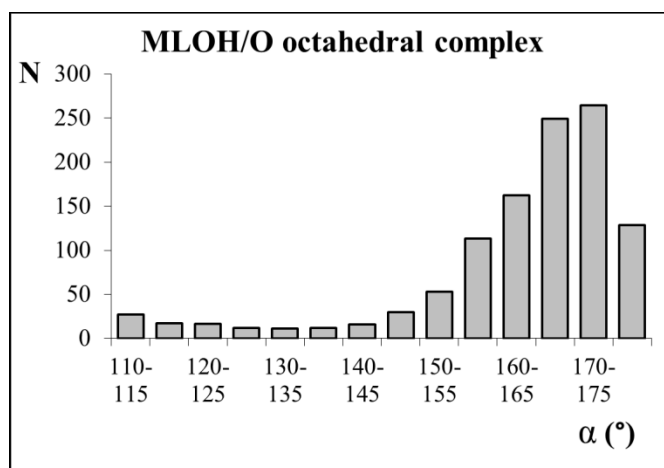


Figure S4. The distribution of cone-corrected angle α (Fig. 3) for octahedral complexes.

[1] J. Kroon and J. A. Kanters, *Nature*, **1974**, 248, 667–669

Correlation between Interaction energies and $V_{S,max}$

Both interaction energies (ΔE) and $V_{S,max}$ for hydrogen-bonded systems, obtained with fixed geometries of monomers, are calculated by using B3PW91/6-31G** for $[ZnCl_2(H_2O)_2]$, $[ZnCl(H_2O)_3]^+$, $[Zn(H_2O)_4]^{2+}$, trans- $[ZnCl_2(H_2O)_4]$, fac- $[ScCl_3(H_2O)_3]$ and mer- $[ScCl_3(H_2O)_3]$ complexes. The correlation between interaction energies and $V_{S,max}$ is very high, the R value is 0.993.

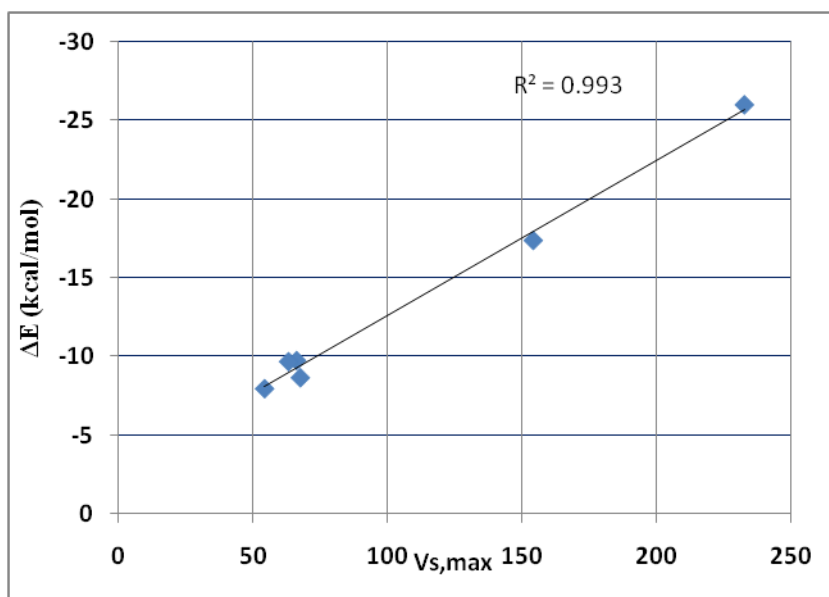


Figure S5. Plot of ΔE vs. $V_{S,max}$ for hydrogen-bonded systems with fixed reactant geometries. The $V_{S,max}$ are for the interacting hydrogens prior to interaction. The correlation coefficient (R) value is 0.993.

The correlation between ΔE and $V_{S,\max}$ for hydrogen-bonded systems obtained with fixed geometries of monomers for $[\text{ZnCl}_2(\text{H}_2\text{O})_2]$, $[\text{ZnCl}(\text{H}_2\text{O})_3]^+$, $[\text{Zn}(\text{H}_2\text{O})_4]^{2+}$, $\text{trans-}[\text{ZnCl}_2(\text{H}_2\text{O})_4]$, $\text{fac-}[\text{ScCl}_3(\text{H}_2\text{O})_3]$ and $\text{mer-}[\text{ScCl}_3(\text{H}_2\text{O})_3]$ complexes is presented for interaction energies calculated at MP2/def2-pvQZ level and $V_{S,\max}$ calculated at B3PW91/6-31G** level. The R value is 0.972.

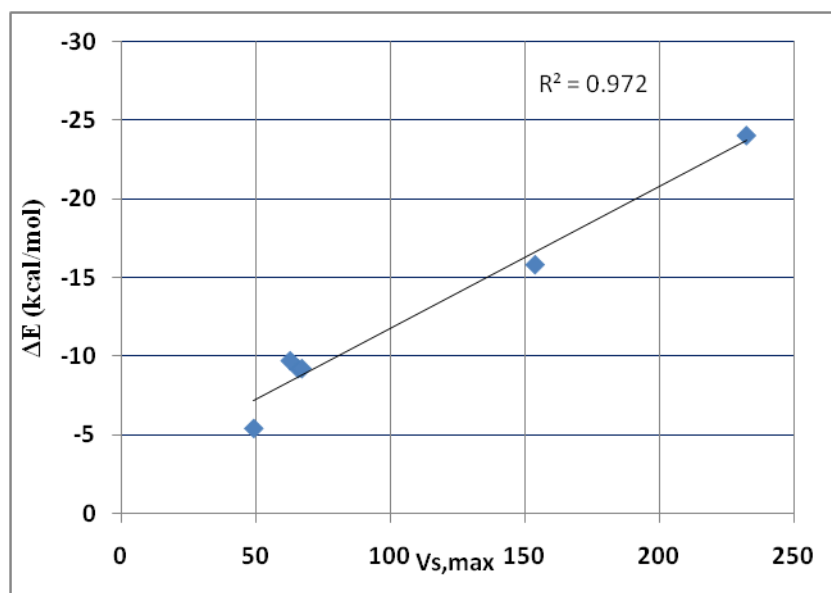


Figure S6. Plot of ΔE vs. $V_{S,\max}$ for hydrogen-bonded systems with fixed reactant geometries. The $V_{S,\max}$ are for the interacting hydrogens prior to interaction. The correlation coefficient (R) value is 0.972.