Can Coordinated Water Be a Good Hydrogen Bond Acceptor?

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Hydrogen bond is arguably the most famous of all noncovalent interactions. The majority of contacts between water molecules in the solid state are hydrogen bonds, with a substantial number of antiparallel dipolar interactions as well.[1] The crystallographic and quantum chemical studies have shown that the strength of hydrogen bonds of water can be increased by metal coordination.[2,3] These previous studies considered coordinated water as hydrogen bond donor. In this study, we wanted to investigate the possibility of coordinated water acting as hydrogen bond acceptor.

The Cambridge Structural Database (CSD) search yielded 1229 hydrogen bonds between coordinated water as hydrogen bond acceptor and uncoordinated water as hydrogen bond donor. These hydrogen bonds are somewhat longer and less directional than hydrogen bonds with donor coordinated water. The strength of these hydrogen bonds was evaluated at the B97D/def2-TZVP level of theory, both on the structures found in the CSD, as well as on the model systems. The obtained energies cover a wide range of values (Figure 1), depending on the charge of the complex, and they can be comparable to the energy of hydrogen bond between two uncoordinated water molecules (-4.84 kcal/mol),[2] or even significantly more favorable if the complex is negatively charged. If the complex is positively charged, these interactions are repulsive (Figure 1), but they are still frequently encountered (444 interactions in crystal structures), simultaneously with other (attractive) interactions.

The strength of interactions shows dependence on the orientation of both hydrogen atoms of uncoordinated water, and it is in general greatly influenced by additional contacts of uncoordinated water with neighboring ligands of the metal complex. Even though it is difficult to estimate how strong these interactions are alone, the calculated interaction energies suggest that coordinated water is a better hydrogen bond donor than hydrogen bond acceptor. However, coordinated water acting as hydrogen bond acceptor gives more opportunities for additional interactions, making the supramolecular systems containing studied hydrogen bonds more stable.

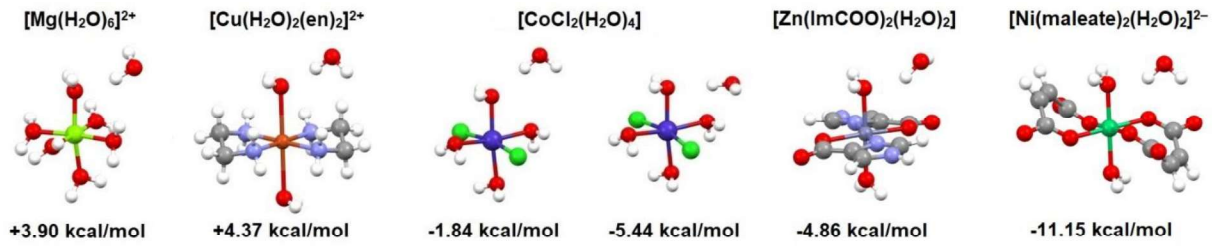

Figure 1. Selected systems with coordinated water as hydrogen bond acceptor; denoted interaction energies were calculated at B97-D/def2-TZVP level

References:

(1) Milovanović, M. R.; Stanković, I. M.; Živković, J. M.; Ninković, D. B.; Hall, M. B.; Zarić, S. D. Water: new aspect of hydrogen bonding in the solid state. *IUCrJ* **2022**, *9*, 639-647. DOI: 10.1107/S2052252522006728.

(2) Andrić, J. M.; Janjić, G. V.; Ninković, D. B.; Zarić, S. D. The influence of water molecule coordination to a metal ion on water hydrogen bonds. *Phys. Chem. Chem. Phys.* **2012**, *14*, 10896-10898. DOI: 10.1039/C2CP41125C.

(3) Andrić, J. M.; Misini-Ignjatović, M. Z.; Murray, J. S.; Politzer, P.; Zarić, S. D. Hydrogen Bonding between Metal-Ion Complexes and Noncoordinated Water: Electrostatic Potentials and Interaction Energies. *ChemPhysChem* **2016**, *17*, 2035-2042. DOI: 10.1002/cphc.201501200.