

Poster

Coordinated water as hydrogen bond acceptor – a joint CSD and DFT perspective

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Hydrogen bond is arguably the most famous type of noncovalent interactions. The prototypical system for studying hydrogen bonds is water dimer, and the strongest hydrogen bond between two water molecules has interaction energy of -5.0 kcal/mol [1]. Upon coordination to metals, electrostatic potentials on hydrogen atoms of water become more positive [2], leading to stronger hydrogen bonds of coordinated water as hydrogen bond donor [2, 3]. Since coordination also leads to less negative electrostatic potentials on water oxygen atom, does it mean that coordinated water cannot be a good hydrogen bond acceptor? Our joint crystallographic and computational study gives insight into this issue.

Cambridge Structural Database (CSD, version 5.43, November 2022) was searched in order to find hydrogen bonds between coordinated water as acceptor and free (uncoordinated) water as donor. The contact between these two entities was characterized as hydrogen bond if O...O distance was shorter than 4.0 Å and O-H...O angle was larger than 110°. By applying these criteria on crystal structures of high quality, a total of 1229 hydrogen bonds were found, and they were divided into two major types (Fig. 1). *Short and linear* hydrogen bonds are the most dominant, and their typical O...H distances are in the range 1.8 Å – 2.1 Å and O-H...O angles in the range 155° – 170° (Fig. 1a). The other type are *long and non-linear* hydrogen bonds, typically with O...H distances in the range 2.8 Å – 3.2 Å and O-H...O angles in the range 110° – 130° (Fig. 1b). Both types of hydrogen bonds are in most cases accompanied by additional interactions, since free water is also in a close proximity to neighbouring ligands of acceptor coordinated water.

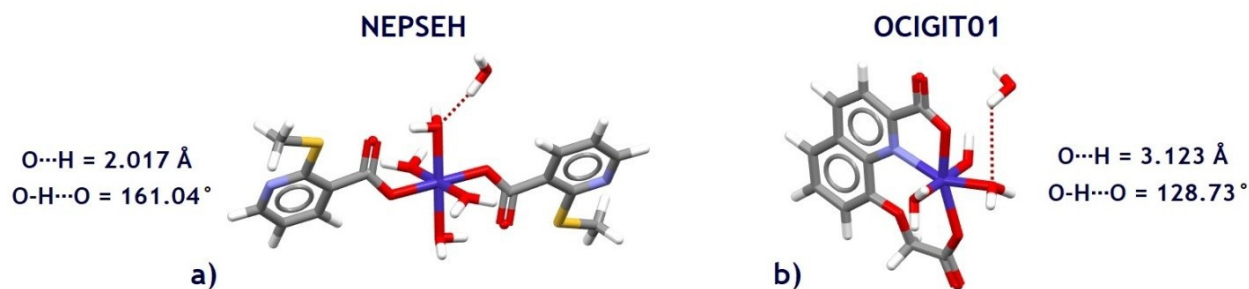


Figure 1. Examples of *short and linear* (a) and *long and non-linear* (b) hydrogen bonds (dashed lines) of coordinated water as hydrogen bond acceptor found in CSD crystal structures; refcodes of crystal structures and geometrical parameters of hydrogen bonds are indicated

DFT calculations were performed at B97D/def2-TZVP level to estimate the strength of hydrogen bonds found in the crystal structures. Hydrogen bonds of acceptor coordinated water were determined to be weaker than hydrogen bonds of donor coordinated water. Moreover, if there are no additional interactions, these hydrogen bonds do not even surpass the interaction energy of free water dimer. However, a vast majority of hydrogen bonds of acceptor coordinated water appear with additional interactions of free water with neighbouring ligands, which can provide additional stabilization. The strongest calculated interaction of a neutral complex has the energy of -9.3 kcal/mol, while interactions of negatively charged complexes are stronger, reaching the energy of -13.2 kcal/mol. These substantial interaction energies suggest that hydrogen bonds of coordinated water as hydrogen bond acceptor are significant contributors to the overall stability of supramolecular structures of metal complexes containing aqua ligands.

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