Are Energies of Hydrogen Bonds of Metal Complexes Predictable? Computational Study in the Gas Phase

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Noncovalent interactions in the second coordination sphere of metal complexes are of great importance for their physical and chemical properties; the ability to predict and tune their energies is essential for many applications, among them catalytic activity [1].

We have performed DFT calculations in the gas phase on hydrogen bonds of 180 aqua and ammine metal complexes to study the various factors that could influence their strengths – charge of the complex, metal oxidation state (OS), metal coordination number (CN), nature of the metal and the other ligands in the complex. In addition, we have studied the nature of these hydrogen bonds by performing the calculations based on Symmetry Adapted Perturbation Theory (SAPT).

The calculations have shown that the strength of hydrogen bonds is dependent only on two factors – the charge of the complex and the ratio of metal oxidation state and metal coordination number (OS/CN); the influence of all other factors is practically negligible [2]. All the complexes with the same charge and OS/CN ratio have very similar energies (Figure 1), as well as the same nature, as evidenced by similarities in their SAPT energy components [2]. Hydrogen bonds become stronger with the increase of positive charge of the complex, as well as the increase of the OS/CN ratio, with both correlations being highly linear [2]. We show that the strength of hydrogen bonds of metal complexes can be predicted solely by knowing their simple descriptors, providing valuable guidelines for the fine tuning of their properties in various applications.

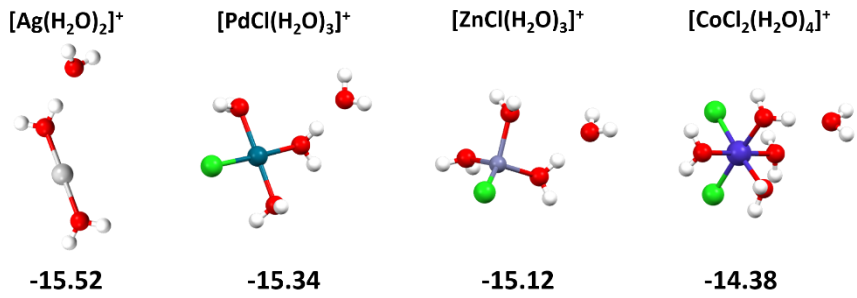

Figure 1. M06L-D3/def2-TZVPP energies (in kcal/mol) of selected hydrogen bonds of 1+ charged complexes with different composition, but the same OS/CN ratio (0.50)

References:

[1] J. N. Reek, B. de Bruin, S. Pullen, T. J. Mooibroek, A. M. Kluwer, X. Caumes, *Chem. Rev.* **122** (2022) 12308-12369.

[2] D. P. Malenov, J. M. Živković, S. D. Zarić, *Dalton. Trans*. **54** (2025) 12754–12759.