

Evidence of strong hydrogen bonding in crystal structures of transition metal complexes

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Hydrogen bonds are of great importance for understanding of different processes in chemistry, crystallography and biology. [1] Properties of hydrogen bonds were subject of numerous experimental and theoretical studies. [1] Specially interesting case represent hydrogen bonds involving transition metal complexes since coordination of ligands can have significant influence on electrostatic potentials of coordinated molecules. [2] Here we present detailed analysis of crystallographic data combined with quantum chemical calculations of very strong hydrogen bonds between water and acetylacetonate ligand of different transition metal complexes.

Cambridge Structural Database (CSD) was searched for all structures containing O-H/O interactions between water molecule and acetylacetonate ligands of transition metal complexes. Geometrical parameters extracted from crystal structures were analyzed and compared with quantum chemical calculations performed on model systems. The O-H/O interactions were studied on model systems containing water and neutral or charged square-planar complexes of Ir, Rh, Pd, and Pt. The strongest interactions were found in charged model systems and these results are in agreement with the predominant electrostatic nature of hydrogen bond (-16.54 kcal/mol). However, surprisingly strong O-H/O interactions were identified also in neutral model systems. The calculated energies of these interactions are -7.98 and -8.22 kcal/mol in [M(acac)(en)]/H₂O (M = Ir(I), Rh(I)) model system, respectively.

Using geometrical criteria for hydrogen bonds 82 structures with 220 O-H/O contacts involving water molecule and coordinated acetylacetonate fragment were found. All extracted structures were statistically analyzed and results of analysis were in agreement with the results of quantum chemical calculations on model systems.

Although the metal is not directly involved in hydrogen bonding, the results of theoretical studies show that the nature of metal atom has significant influence on the strength of hydrogen bonds of ligands.

[1] T. Steiner, *Angew. Chem. Int. Ed.*, 2002, 48-76.

[2] G. V. Janjić, M. D. Milosavljević, D. Ž. Veljković, S. D. Zarić, *Phys. Chem. Chem. Phys.*, 2017, 8657-8660.

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