

Influence of Coordination on OH/ π and NH/ π Interactions

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Abstract: The interactions of noncoordinated water or ammonia molecules with aromatic rings, as well as coordinated water or coordinated ammonia molecules with aromatic rings have been investigated by searching the Cambridge Structural Database (CSD) and through quantum-chemical calculations. The data from the CSD show that for noncoordinated systems distances between the interacting fragments are the shortest in case of negative C₆-aromatic groups and the longest in case of positive C₆-aromatic groups. In the case of contacts between coordinated water or ammonia molecules and C₆-aromatic group, oppositely charged fragments are mutually closer than the neutral fragments. The DFT calculations for the water/benzene system yield an interaction energy of -2.97 kcal/mol, while for the [Zn(H₂O)₆]²⁺/C₆H₆ system the interaction energy is -14.72 kcal/mol. For the ammonia/benzene system, the DFT calculations yield an interaction energy of -2.28 kcal/mol, while for the [Zn(NH₃)₆]²⁺/C₆H₆ system it is -15.50 kcal/mol. The results show that there is an influence of water or ammonia coordination on OH/ π or NH/ π interactions; the interactions of coordinated species are significantly stronger. OH/ π and NH/ π interactions are comparable in both cases. OH/ π interactions are slightly stronger than NH/ π interactions in the case of noncoordinated molecules due to a higher partially positive charge on the hydrogen atom of the water molecule, but this is not necessarily the case for the coordinated molecules due to additional interactions that can occur between the benzene ring and the other ligands present in the complex.

Keywords: OH/ π interactions, NH/ π interactions, CSD, quantum chemical calculations non-covalent interactions, metal complexes

1. Introduction

Interaction of water molecules with aromatic systems is of large importance in many systems from biological molecules to materials. The results show the influence of water coordination to a metal ion on OH/ π interactions; interactions of coordinated water are significantly stronger even if the aqua complex is neutral [1]. Aromatic ring/ammonia dimers are also well studied systems. NH/ π interactions of the coordinated ammonia

were studied by analyzing crystal structures deposited in the Cambridge Structural Database (CSD) and by quantum chemical calculations [2].

2. Methodology

The Cambridge Structural Database (CSD) was searched for the intermolecular OH/ π and NH/ π interactions of the noncoordinated and coordinated water or noncoordinated and coordinated ammonia with C₆-aryl groups. The structure was considered a hit if the distance (*d*) between the interacting hydrogen atom H_i and the center of the C₆-aryl ring (Ω) was less than 3.5 Å, the angle α was larger than 110° and the angle β smaller than 30° for water/C₆-aryl contacts (Figure 1a), or the distance *d* was smaller than 4.5 Å, the angle α was between 90 and 180° and the angle β was smaller than 50° for ammonia/C₆-aryl contacts (Figure 1b).

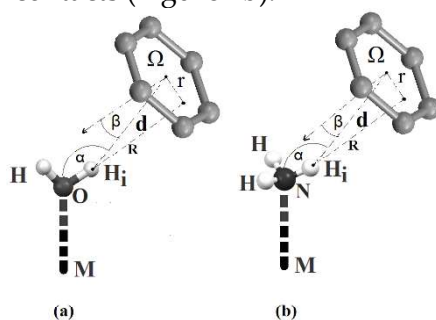


Figure 1. The geometric parameters describing OH/ π and NH/ π interactions of the water and ammonia in case of the noncoordinated molecules and the molecules coordinated to any metal atom (*M*). Ω is the center of the aromatic ring, *d* is the distance between Ω and hydrogen atom H_i of water or ammonia molecule. α is the O–H_i⋯ Ω angle for coordinated and noncoordinated water systems and N–H_i⋯ Ω angle for coordinated and noncoordinated ammonia systems, β is the angle between the H_i⋯ Ω direction and the normal to the C₆-aryl ring passing through the ring center Ω . The offset *r* is the distance between the ring center Ω and the projection of the H_i atom on the ring plane. *R* is the normal distance between H_i atom and the ring plane.

In order to obtain interaction energies of the noncoordinated and coordinated water and ammonia molecules with the benzene ring we performed the calculation of the interaction energy on model structures given in Figure 2. The energies are calculated using a Gaussian series of programs [3] at B3LYP/def2TZVP level with a D3 version of Grimme dispersion with Becke-Johnson damping [4] and the basis set superposition error correction included [5].

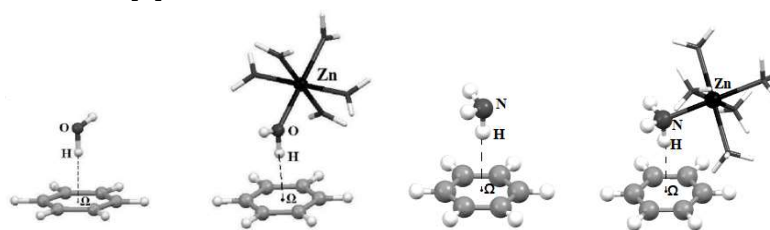


Figure 2. Model systems for OH/ π interactions of the coordinated and noncoordinated water and NH/ π interactions of the coordinated and noncoordinated ammonia used for calculations.

3. Results

Since charge of the interacting species have influence on OH/ π interactions, 644 interactions of noncoordinated water that are found by the CSD search were separated into three groups depending on the charge of the species. There is a tendency towards shorter d distances if the aryl groups are negative. The distances d are the longest for positive aryl groups. The contacts between the coordinated water molecule and the C₆-aryl group were separated into two groups, a group of 71 contacts with neutral species and a group of 54 contacts where both aqua complex and aryl group are charged. Shorter d distances in systems with opposite charge indicate stronger interactions than in the case of neutral species [1].

We found 41 contacts of noncoordinated NH₃ molecule and a C₆-aryl ring and 332 contacts with only one amine ligand interacting with a C₆-aryl ring. The distribution of the distance d for NH/ π interactions indicates that these distances are longer in systems with a neutral aryl group. When the aryl group is a part of a negative species, the distances are shorter. The shortest distance d for the contacts between the coordinated ammonia and the C₆-aryl group are found in the systems with oppositely charged species, which indicates significantly stronger interactions. Comparison of NH/ π of coordinated and noncoordinated ammonia shows that the interacting H_i atoms are closer to the aryl group when the amine group is coordinated [2].

The calculation results show that the coordination of both water and ammonia molecules to a metal substantially strengthens the interactions with benzene. Namely, the interaction energies of noncoordinated water and ammonia molecules are -2.97 kcal/mol and -2.28 kcal/mol, respectively, while for the coordinated water and ammonia the interactions are much stronger, -14.72 and -15.50 kcal, respectively (Table 1). OH/ π interaction in water/benzene and NH/ π interaction in ammonia/benzene systems are of comparable strength, although OH/ π interaction is slightly stronger (Table 1) due to higher electronegativity of the oxygen than the nitrogen atom, which leads to the more partially positive interacting hydrogen atom. Aqua and amine complexes also form similarly strong OH/ π and NH/ π interactions (Table 1), but the interactions are more difficult to compare in this case due to the presence of side interactions between the benzene ring and the other ligands present in the metal complex. The side interactions are more pronounced in the amine complex, which leads to a slightly stronger interaction (-15.50 kcal/mol, Table 1).

Table 1. Interaction energies (ΔE) and normal distances (R) for the most stable dimers of the noncoordinated and coordinated water and ammonia molecules and the benzene molecule.

Model systems	ΔE (kcal/mol)	R (Å)
H ₂ O/C ₆ H ₆	-2.97	2.7
[Zn(H ₂ O) ₆] ²⁺ /C ₆ H ₆	-14.72	2.3
NH ₃ /C ₆ H ₆	-2.28	2.6
[Zn(NH ₃) ₆] ²⁺ /C ₆ H ₆	-15.50	2.4

4. Conclusions

In summary, the results show a significant influence of charge of the interacting fragments on OH/ π and NH/ π contacts in the CSD, since distances between the interacting fragments are the shortest in the case of negative aryl groups interacting with water and ammonia molecules and the longest in case of positive aryl groups. Oppositely charged species are closer than neutral species in the CSD in case of contacts between the coordinated water or ammonia molecules and the aryl group. The calculated interaction energies on dimer model systems are much higher in the case of the coordinated water and ammonia molecules. OH/ π and NH/ π interactions are of comparable strength for the noncoordinated as well as for the coordinated molecules. Partial charge is more positive on hydrogen atoms of the water molecule than the ammonia molecule, which leads to a slightly stronger interaction. Although the interaction is slightly stronger in the case of amine than the aqua complex, these interactions are more difficult to compare due to the additional interactions of the benzene ring with the other ligands present in the metal complex.

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