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C – H···π INTERACTIONS IN THE METAL-PORPHYRIN COMPLEXES WITH CHELATE RING AS THE H ACCEPTOR

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Abstract

Specific C – H···π interactions with the π-system of porphyrinato chelate ring were found in crystal structures of transition metal complexes from the CSD and statistical analysis of geometrical parameters for intramolecular and intermolecular interactions was done. DFT calculations on a model system show that energy of the interaction is 1.58 kcal/mol and that the strongest interaction occurs when the distance between hydrogen atom and the center of the chelate ring is 2.6 Å. This prediction is in good agreement with the distances for intermolecular interactions found in the crystal structures. In many cases the intramolecular interaction distances are much shorter than 2.6 Å, and these short distances appear to be caused by geometrical constrains. The C – H···π interactions with chelate ring of porphyrinato ligand can be important in biomolecules with porphyrin as they can influence the structure, contribute to the stability and play some role in function of biomolecules.

Introduction

Noncovalent interactions of π–systems have been extensively studied in recent years, and their importance has been shown in different molecular systems from molecular biology to crystal engineering. X – H···π interactions in metal complexes including organometalics, have been found by searching databases of crystal structures, and investigated by both quantum chemical calculations and spectroscopic methods. C – H···π interactions are the weakest among the X – H···π interactions. However, C – H groups are very abundant and these interactions appear frequently, hence they are important for molecular recognition.

Recently, a few studies of noncovalent interactions with chelate ring as a π–system were published [1-3]. In our previous study structural and computational evidence was given for a particular type of C – H···π interaction where the hydrogen atom interacts with a chelate ring [1]. The Cambridge Structural Database (CSD) was screened in order to find C – H···π interactions with a six-membered chelate ring with delocalized bonds. It was shown that there is large number of structures with short distances between the interacting hydrogen atom and the center of the chelate ring (< 3.0 Å) and with C – H line almost perpendicular to the center of the chelate ring. Calculations of these interactions by density functional theory (DFT) show energies of interaction of about 1 kcal/mol [1]. The calculated energies and observed geometries are

comparable to those of C – H···π interactions where the proton acceptor is an organic aromatic ring.

Porphyrin molecule and derivatives of porphyrine possess four pyrole rings with delocalized π–systems. When porphyrin is coordinated as a tetradentate ligand to a metal, additional rings with delocalized π–bonds are formed four six-membered chelate rings. These chelate ring π–systems of the coordinated porphyrin can be involved in C – H···π interactions.

Here, we present the first results and analysis on C – H···π interactions in porphyrinato complexes where the π–systems of the six-membered chelate rings have role of a π–systems.

Results and Discusion

The structures of metal complexes with coordinated derivatives of porphyrin were screened using the same geometric criteria as in the previous work [1] described briefly below. We searched CSD for structures with hydrogen atom to center of the six-membered ring (Ω) distances shorter than 3.0 Å, and with a X-H···Ω axis in a narrow cone perpendicular to the ring ($\alpha > 110°$, $\beta < 16°$) (Fig. 1).
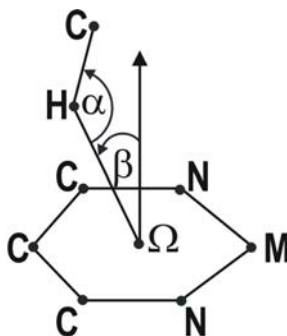

Figure 1. Geometrical parameters for the C – H···π interaction with the chelate ring of the porphyrinato ligand.

In searching crystal structures of transition metal complexes from the Cambridge Structural Database (CSD) for specific C – H···π interactions, interactions between C – H groups and the π-system of porphyrinato chelate rings in metal complexes, we found 655 such interactions. Among them, 411 are intermolecular and 244 are intramolecular. As can be anticipated from steric considerations, intermolecular C – H···π interactions are possible only in metal complexes with a vacant axial position. For intermolecular interactions, most of the examples are found for complexes with Zn (122), Ni (74), Fe (69) and Cu (36), while for intramolecular C – H···π interactions, most of the examples are found for complexes with Fe (116), Zn (37) and Ru (33). The differences in the distributions of geometrical parameters for intramolecular and intermolecular interactions can be explained by geometrical constrains in the in-

tramolecular interactions, where in most of these cases the hydrogen atom that interacts with the chelate ring is part of the axial ligand.

The calculations have been done using DFT method (B3LYP). Calculations were performed with GAUSSIAN98 program. The LANL2DZ basis set was chosen for the copper atom and 6-31G** basis sets were chosen for the carbon, nitrogen and hydrogen atoms. The bonding energies were calculated as the difference between the energy of the $[Cu(por)] - C_2H_2$ system and the sum of the energies of the $[Cu(por)]$ complex and acetylene. Single point calculations have been done for different H···Ω distances from 1.8 – 3.4 Å. For distances below 2.0 Å, the interaction is repulsive. At a distance of 2.3 Å, the interaction energy is greater than 1 kcal/mol. The minimum occurs at 2.6 Å, and the energy of interaction for this structure is 1.58 kcal/mol. The minimum is shallow and the interaction energy is greater than 1.5 kcal/mol for the range of 2.4 – 2.9 Å, while it is greater than 1 kcal/mol to 3.4 Å. Hence, there is attractive interaction even at the distances longer than 3.0 Å. The calculated energies for the interaction at different distances is in good agreement with the distances for the intermolecular interactions found in the crystal structures.

Conclusion

The study shows that chelate rings of coordinated porphyrin can be hydrogen acceptors in C – H···π interactions. In searching crystal structures of transition metal complexes with porphyrin from the CSD, 655 C – H···π interactions (411 intermolecular and 244 intramolecular) were found. Statistical analysis show that there are different distributions of geometrical parameters for intramolecular or intermolecular interactions, caused by geometrical constrains for the intramolecular interactions. DFT calculations on a model system show that energy of the interaction is 1.58 kcal/mol and that the strongest interaction occurs when the distance between hydrogen atom and the center of the chelate ring is 2.6 Å. This prediction is in good agreement with the distances for intermolecular interactions found in the crystal structures. In many cases the intramolecular interaction distances are much shorter than 2.6 Å, and these short distances appear to be caused by geometrical constrains.

The C – H···π interactions with chelate ring of porphyrinato ligand can be important in biomolecules with porphyrin as they can influence the structure, contribute to the stability and play some role in function of biomolecules.

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