Evidence Based on Crystal Structures and Calculations of a C−H···π Interaction Between an Organic Moiety and a Chelate Ring in Transition Metal Complexes

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Structural and computational evidence is given for a special type of C–H···π interaction where the C–H group interacts with the π-system of a six-membered chelate ring. An investigation of crystal structures shows that these interactions take place in quite a number of metal complexes, including organometallic compounds; in the CSD we found over 1200 structures with these interactions. These interactions exist in complexes of different metals and various chelate rings. DFT calculations on three model systems show that the energy of these interactions is about 1 kcal/mol.

Introduction

Noncovalent interactions involving π-systems have been extensively studied in the last few years and the importance of these interactions has been shown in different molecular systems from molecular biology to crystal engineering.[1−8]

Noncovalent interactions in metal complexes between π-systems and ligands with X−H groups (X = N, O, C) have been found and investigated by searching databases of crystal structures[9−11] and by quantum chemical calculations.[11−14] It has been shown that these interactions play a role in crystal engineering[7−9] and in the stability of metalloproteins, and it has been proposed that they can play a role in the mechanism of enzymatic reactions.[10] In metal complexes, the partial positive charge of the hydrogen atom belonging to the ligand, gained upon coordination to the metal cation, makes the interactions with the π-system stronger.[8−14] The stabilization energy of the metal ligand aromatic cation − π (MLAC-π) interactions in crystal structures, where ligands coordinated to a metal interact with aromatic groups, was evaluated by quantum chemical calculations to be between 4 and 10 kcal/mol.[10,11]

C−H···π interactions are the weakest among X−H···π interactions. C−H groups are very abundant in organic and biomolecules therefore these interactions appear very frequently and are very important for molecular recognition.[6,15,16] Theoretical calculations have shown the energy and the nature of these interactions,[6,15−18] leading to calculated values close to 1 kcal/mol. C−H···π interactions have also been found in metal complexes.[9,11,16,19−23] However, a C−H···π interaction, where a C−H group belonging to an organic moiety interacts with the π-system of a chelate ring containing a metal atom, have not been reported before. In this article we will give evidence for this type of interaction.

Results and Discussion

Searching crystal structures of transition metal complexes from the Cambridge Structural Database (CSD) shows that specific C−H···π interactions — interactions between C−H groups and the π-systems of chelate ring — can be observed in many crystal structures. It is supposed that the metal atom in these chelate rings is involved in π-delocalisation.[24] In the CSD, we found 5091 structures containing almost planar chelate rings, with delocalised π-bonds. Among these structures, there are 1265 structures[25] with a weak C−H···π interaction ($\alpha > 110°$, $\beta < 16°$, and H···Ω distance < 3.0 Å; α, β, and Ω are defined in Figure 1) and 151 structures with a very strong interaction ($\alpha > 145°$, $\beta < 12°$, and H···Ω distance < 2.6 Å). For many of these structures there is more than one interaction per molecule. The geometrical parameters for some examples are shown

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in Table 1. All these examples have a very short H···Ω distance (H···Ω < 2.6 Å), the H atom is almost centered over the chelate ring center (β < 12.5°) and the X−H···Ω line is not too bent (α < 145°). From a geometrical point of view, interactions in these structures are similar to strong C−H···π interactions in organic molecules.[6,16] An example from Table 1 is shown in Figure 2.

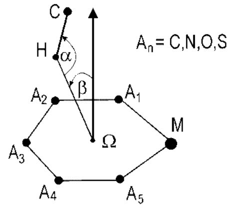

Figure 1. Geometric parameters used for the determination of the C−H···π interaction

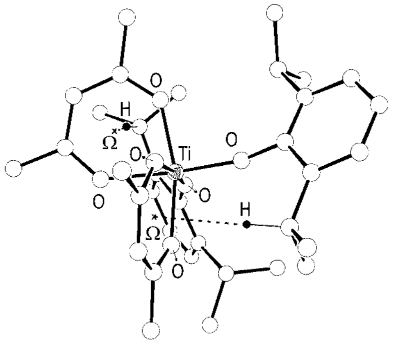

Figure 2. Perspective view of ACIPTI[26] as a selected example for a C−H···π interaction with the π-system of the chelate rings; the carbon atoms are unlabelled

From Table 1, it is clear that these interactions occur in metal complexes — including organometallic compounds — of different metals and various chelate rings. In the interactions shown in Table 1, some of the C donor atoms are sp^3 hybridized and some of them are sp^2. For all the C_{sp^3} cases, the carbon atom is bonded to two or three other non-hydrogen atoms, therefore the position of the H atom which is directed toward the chelate ring is reliable. Most of these interactions are intermolecular, and only the ACIPTI compound presents an intramolecular interaction.

It is very interesting to notice that in all the examples shown in Table 1 the complexes are neutral and both the chelate ring and the C−H group are in the same molecule. In the case of intermolecular interactions, the interaction occurs between two identical molecules: the C−H group from one molecule interacting with the chelate ring from the other molecule. For this type of interaction, we assume that the neutrality of the complexes is important, as, on the one hand, the chelate ring should not have any partial positive charge, which would be the case if the complex were positively charged, and, on the other hand, the π-system from the chelate ring should not interact with a negatively charged complex. In the case of a neutral complex the interacting H atom has a partial positive charge, which is enough for a weak C−H···π interaction.

Table 1. Selected crystal structures of metal complexes where a C−H group interacts with the π-system of a chelate ring[a]

CSD refcode	α (°)[b]	β (°)[c]	H···Ω[d] (Å)	C···Ω (Å)	Chelate ring	D[e]	*R* (%)[f]	ref.
ACIPTI	165.3	2.0	2.43	3.51	TiOCCCO	C_{sp^3}	6.60	26
BEPZOL	175.6	3.8	2.48	3.56	CuNCNCN	C_{sp^3}	3.20	27
COTQAD	155.1	1.2	2.38	3.39	ZrNCCCN	C_{sp^2}	4.03	28
COTQEH	155.2	0.6	2.36	3.38	HfNCCCN	C_{sp^2}	2.63	28
FEBTAH	167.7	1.4	2.39	3.45	NiNCCCN	C_{sp^3}	3.00	29
GORYER	176.6	1.6	2.46	3.54	MnOCCCN	C_{sp^3}	5.23	30
GOXDAY	150.9	5.0	2.48	3.46	FeNCCCN	C_{sp^2}	5.80	31
HALWAS	146.8	3.9	2.40	3.36	ZnNCCCN	C_{sp^2}	4.10	32
HAMDAA	148.8	3.7	2.40	3.38	ZnNCCCN	C_{sp^2}	7.40	32
HAMGUX	148.9	4.7	2.46	3.43	ZnNCCCN	C_{sp^2}	5.20	32
JOXGIM	158.1	6.2	2.59	3.68	CuOCCCN	C_{sp^3}	5.80	33
LICSEV	154.2	4.7	2.31	3.32	CuNCCCN	C_{sp^3}	6.59	34
LOFZOV	150.5	3.4	2.36	3.35	NiOCCCN	C_{sp^2}	4.27	35
MAMTOJ	165.8	5.3	2.46	3.52	CoOCCCN	C_{sp^2}	3.54	36
MAMTUP	167.1	1.0	2.32	3.38	CuOCCCN	C_{sp^3}	5.09	36
PIQZUK	175.1	4.7	2.45	3.53	ReOCCCN	C_{sp^2}	3.71	37
SUMXIH	145.7	5.1	2.50	3.45	FeNCCCN	C_{sp^3}	3.61	38
VAFQIC	173.5	3.6	2.30	3.38	ZnNCCCN	C_{sp^2}	4.90	39
YINLUC	159.1	3.1	2.54	3.60	NiOCCCO	C_{sp^2}	3.70	40
ZAXDOR	155.9	5.3	2.30	3.31	ZnOCCCN	C_{sp^3}	3.57	41
ZONQOI	149.4	4.4	2.34	3.32	CoNCCCN	C_{sp^2}	7.20	42
ZOPYUY	157.4	12.4	2.34	3.37	CuOCCCN	C_{sp^3}	3.80	43

[a] Data for normalised H-atom positions. [b] α is the C−H···Ω angle (Figure 1). [c] β is the angle between the normal of the chelate ring and the Ω···H line (Figure 1). [d] H···Ω is the distance between the normalised H-atom position and the center of the ring (Figure 1). [e] C_{sp^2} is bonded to two non-hydrogen atoms. C_{sp^3} is bonded to two or three non-hydrogen atoms. [f] *R* is the reliability factor taken from CSD.

In order to evaluate the energy of this type of interaction, DFT calculations were performed on model systems made from the structures JOXGIM, YINLUC and ZOPYUY. Since the molecules in which these interactions occur are rather large, and there are at the same time other intermolecular interactions, we chose the structures where we were able to separate the C−H···π interaction from other interactions, and the calculations were performed on smaller model systems. These model systems were built from the crystal structures by substituting all groups that are not important for the interaction with hydrogen atoms. The model systems for YINLUC and ZOPYUY contain two complex molecules that interact with each other, whereas the model system for JOXGIM has one complex molecule interacting with a molecule of methane (Figure 3). In the JOXGIM model system we used a methane molecule instead of the second molecule of complex as other intermolecular interactions could exist between two complex molecules in the crystal structure, and therefore the calculated energy of interaction of these two molecules would not be only the energy of the C−H···π interaction. The geometries of the interactions were kept the same as they were in the crystal structures. The calculated energies of interactions are 0.89, 1.33, and 1.38 kcal/mol for model systems from JOXGIM, YINLUC and ZOPYUY, respectively. The calculated energies depend upon the H···Ω distance: the distance is the largest in JOXGIM and the shortest in ZOPYUY (Table 1). The calculated values for interacting energies are similar to calculated values of C−H···π interactions in organic molecules.[6]

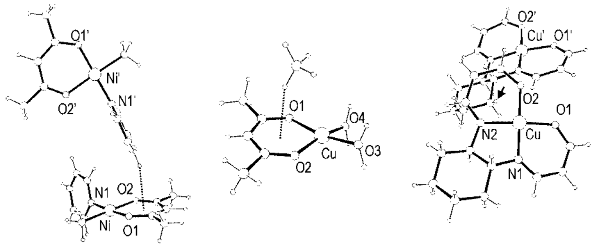

Figure 3. Model systems used for DFT calculations of the energy of C−H···π interactions with a chelate ring; YINLUC (left), JOXGIM (middle), ZOPYUY (right); the carbon atoms are unlabelled

Conclusion

The results presented here show that there is another noncovalent interaction that cannot exist in organic molecules but only in metal complexes. This interaction, where metal-containing chelate rings can be involved in C−H···π interactions, is widespread in metal complexes, including organometallic compounds. It has been estimated by DFT calculations that the energy of this interaction is about 1 kcal/mol. This kind of interaction, like other noncovalent interactions, can be used in nonorganic crystal engineering to design crystals with desired structures and properties. We are continuing our extensive investigations into this kind of interaction using a more detailed analysis of crystal structures from the CSD, enhanced by quantum chemical calculations.

Data Screening and Computational Methods

The Cambridge Structural Database (CSD)[44] was screened in order to find C−H···π interactions with a chelate ring. We searched for the crystal structures of metal complexes that have six-membered, almost-planar chelate rings with delocalized bonds and with N, S, or O atoms coordinated to a transition metal atom, and we found 5091 such structures. In these structures we demanded that there is an hydrogen atom at a distance shorter than 3.0 Å from Ω, the center of the six-membered ring, and presenting an X−H···Ω axis in a narrow cone perpendicular to the ring ($\alpha > 110°$, $\beta < 16°$) (Figure 1). These screening criteria are more restrictive than criteria used previously for similar screenings.[45,46] All C−H distances were normalized to 1.083 Å. In this way we obtained 1265 crystal structures.

Quantum chemical calculations were performed on model systems built from crystal structures using the B3LYP method and 6−31g** basis set on all atoms, except for the metal atoms, where the LANL2DZ basis set was used. The calculations were perfomred with Gaussian-98.[47]

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