

Parallel stacking interactions in square-planar transition-metal complexes containing fused chelate and C₆-aromatic rings

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Stacking interactions in the crystal structures of square-planar transition metal complexes from the Cambridge Structural Database with five- and six-membered chelate rings fused with C₆-arom rings (arom = aromatic) were analyzed. The distribution of distances between the closest C₆-arom–C₆-arom and C₆-arom–chelate contacts shows that in a large fraction of the intermolecular interactions the C₆-arom ring of one molecule is closer to the chelate than to the C₆-arom ring of the other molecule. These results indicate a possible preference of the C₆-arom ring to form stacking contacts with the chelate rings. The preference is ubiquitous and does not depend on the metal type.

1. Introduction

Recently the stacking interactions of aromatic and other π -systems have been intensively studied (Sponer *et al.*, 2008; Anzellotti *et al.*, 2008; Wang *et al.*, 2008; Bugarcic *et al.*, 2008; Ostojić *et al.*, 2008; Janjić *et al.*, 2010; Hohenstein & Sherrill, 2009; Bates *et al.*, 2008). Interactions in systems involving metal atoms and phenyl rings have received considerable attention after their description in terms of cation- π interactions (Ma & Dougherty, 1997; Schmitt *et al.*, 2003; Lovell *et al.*, 2003; Zhu *et al.*, 2003; Kim *et al.*, 2003; Zarić, 1999; Zarić *et al.*, 2000). In the last decade the approach to this problem has been extended to include metal-containing cyclic fragments (chelate rings). The first investigations of metal–aryl interactions focused on the contacts between the metal and the closest C atom from the arom ring (Costa-Filho *et al.*, 2001). The latter research has pointed out that the presence of the chelate ring influences the metal–aryl contact, suggesting the existence of stacking interactions between the chelate ring and the aryl ring. In our previous work (Tomić *et al.*, 2003, 2004) we have shown that the copper(II)–aryl contacts were a consequence of stacking interactions between the chelate and aryl rings. By extending that work to include complexes of all the transition metals, the chelate–aryl stacking arrangements were found for various types of metal chelates, showing that the chelate ring has a tendency of making the stacking interaction with the phenyl ring independent of metal type in the chelate ring (Tomić *et al.*, 2006; Sredojević *et al.*, 2007). In transition metal complexes planar chelate rings with delocalized π -bonds can form stacking interactions (Costa-Filho *et al.*, 2001; Tomić *et al.*, 2003, 2004, 2006; Sredojević *et al.*, 2007) similar to those of aromatic organic molecules (Lee *et al.*, 2007; Sinnokrot & Sherrill, 2006; Podeszwa *et al.*, 2006; Pitonak *et al.*, 2008; Janowski & Pulay, 2007). These observations could be connected with speculations of aromatic character in planar chelate rings with delocalized π -bonds (Milčić *et al.*, 2007).

Planar chelate rings with delocalized π -bonds can also form CH/ π interactions (Milčić *et al.*, 2006; Bogdanović *et al.*, 2002; Medaković *et al.*, 2004). We investigated the tendency of the chelate ring to stack and the CH/ π interactions with the phenyl ring. Analysis (Sredojević *et al.*, 2007) showed that stacking interactions between planar chelate and aryl rings are preferred to CH/ π interactions. The other factor with the potential to influence the chelate–phenyl stacking is the presence of an organic aromatic system which could compete with the chelate ring for the formation of stacking contacts. In this article we are trying to tackle that problem by investigating the stacking contacts in square-planar complexes, where the $C_{6\text{-arom}}$ ring is fused with the chelate ring. We analyzed the data in crystal structures from the Cambridge Structural Database (CSD), since this enables intra- and intermolecular interactions to be studied (Weng *et al.*, 2008; Galek *et al.*, 2007; van de Streek & Motherwell, 2005; Orpen, 2002).

2. Methodology

A Cambridge Structural Database (Allen, 2002; November 2011) search was performed using the *Quest3D* program (Bruno *et al.*, 2002) to extract all structures of square-planar transition metal complexes containing five- or six-membered chelate rings fused with the $C_{6\text{-arom}}$ ring (Fig. 1). To obtain square-planar metal complexes with planar chelate rings we used the same criteria as used before in similar studies (Tomić *et al.*, 2004, 2006, Sredojević *et al.*, 2007). The metal atom is coordinated by exactly four atoms according to the criteria used in the CSD system. To ensure relative planarity of the complex molecule, the *trans* angles formed by the metal and coordinated atoms have been restricted to lie between 150 and 180°. To ensure planarity of the chelate rings only those having absolute values of the endocyclic torsion angles not exceeding 5° have been considered. From visual inspections we find that all the complexes obtained were square planar. Analyses revealed that all C, N and O atoms are sp^2 -hybridized, except in a few structures (OGAHEK, TIXTUP – Nsp^3 ; GEVJAS, PORNOA, TORYUU – Csp^3) the S atom can be sp^2 or sp^3 hybridized, and P atoms are sp^3 -hybridized in all cases. To minimize the factors influencing the association of molecules and to limit our study to neutral complexes we performed our

analysis exclusively on single-component crystals, *i.e.* crystals containing solely the uncharged complex molecules. In this way the possible influence of the organic aromatic solvent molecules included in the crystal lattice on the interactions studied was avoided.

In order to find the intermolecular parallel stacking interactions of rings in the complexes we used only those structures where the dihedral angle (φ) between the mean planes of the fragments is lower than 20°, and the angle between the normal to the $C_{6\text{-arom}}$ ring and the line that connect the centers of the chelate and $C_{6\text{-arom}}$ rings (β_{CA}), or centers of two $C_{6\text{-arom}}$ rings (β_{AA}) is lower than 35°. Polymeric, disordered and structures with a crystallographic *R* factor greater than 0.10 were excluded.

We looked for intermolecular parallel stacking interactions of the $C_{6\text{-arom}}$ ring of one complex with a chelate and $C_{6\text{-arom}}$ rings of the other complex using the criteria that the distance between the centroids of $C_{6\text{-arom}}$ and $C_{6\text{-arom}}$ or $C_{6\text{-arom}}$ and chelate rings is smaller than 4.6 Å (Janiak, 2000).

3. Results and discussion

The Cambridge Structural Database was searched for square-planar complexes with five- and six-membered chelate rings fused with the $C_{6\text{-arom}}$ ring. We found two such fragments for five-membered chelate rings (fragments 1 and 2) and one for six-membered rings (fragment 3; Fig. 1). These three fragments were used in the analysis. Other chelate or aromatic rings were allowed in the molecule, some being fused with the chelate and/or $C_{6\text{-arom}}$ rings of the fragments.

We looked for intermolecular parallel stacking interactions of the $C_{6\text{-arom}}$ ring of one complex with a chelate and $C_{6\text{-arom}}$ rings of the other complex satisfying the general criteria for interactions, *i.e.* the distance between the centroids of the relevant rings are lower than 4.6 Å. It is possible to have structures where the centroid of the $C_{6\text{-arom}}$ ring has intermolecular distances shorter than 4.6 Å with both chelate and $C_{6\text{-arom}}$ rings. In such cases we accepted the lowest centroid–centroid distance as the one associated with the stronger interaction. To encompass all the possibilities for $C_{6\text{-arom}}$ –chelate and $C_{6\text{-arom}}$ – $C_{6\text{-arom}}$ interactions we performed two separate searches. In the first search the distances between the

centers of the chelate (Ω) and the $C_{6\text{-arom}}$ group (Ω') were restricted to be shorter than 4.6 Å, and the β_{CA} angle restricted to be smaller than 35°. In the second search the distances between the centers of two $C_{6\text{-arom}}$ groups (Ω'') were restricted to be shorter than 4.6 Å, and the β_{AA} angle restricted to be smaller than 35°. A schematic representation is shown in Fig. 2. The results from two searches were joined and data belonging to both data sets were separately analyzed

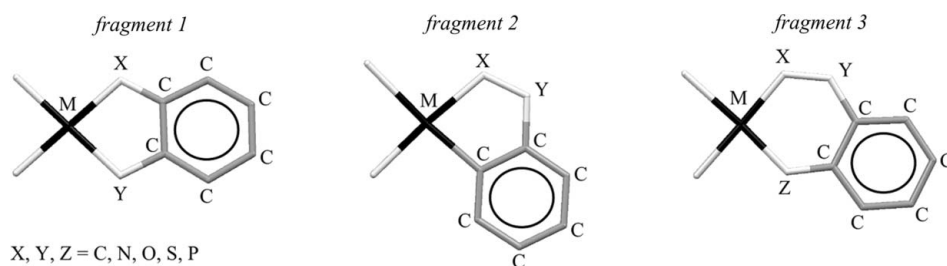


Figure 1

Fragments of square-planar complexes with five- (fragments 1 and 2) and six-membered (fragment 3) chelate rings fused with a $C_{6\text{-arom}}$ ring, used to study the intermolecular parallel stacking interactions of the $C_{6\text{-arom}}$ ring.

to eliminate duplicate entries. The resulting data set was used in further analysis.

In the CSD we found 371, 438 and 282 structures containing fragments 1, 2 and 3, respectively. Among these structures we found parallel stacking interactions in 106, 94 and 85 crystal structures containing fragments 1, 2 and 3, respectively. In the structures with fragment 1 we found 126 contacts, in structures with fragment 2 there were 153 contacts, while in structures with fragment 3 we found 94 contacts.

In order to compare the intermolecular stacking interactions of the $C_{6\text{-arom}}$ ring with the chelate and the $C_{6\text{-arom}}$ ring of the other complex we inspected distances between the centroids of the chelate and the $C_{6\text{-arom}}$ rings (D_{CA}), and distances between the centroids of two $C_{6\text{-arom}}$ rings (D_{AA}). The difference between these two distances ($\Delta = D_{AA} - D_{CA}$) was used to find the shorter centroid–centroid distance. The positive value of the Δ parameter indicated that in the intermolecular interaction the $C_{6\text{-arom}}$ ring of one molecule was closer to the chelate than to the $C_{6\text{-arom}}$ ring of the other molecule. A schematic presentation of the parameters used is shown in Fig. 3. When the $C_{6\text{-arom}}$ ring is in a *face-to-face* stacking orientation with respect to the other $C_{6\text{-arom}}$ ring the value of the Δ parameter is about -0.7 \AA , while for the *face-to-face* stacking orientation between the $C_{6\text{-arom}}$ ring and the chelate ring Δ is *ca* 0.7 \AA .

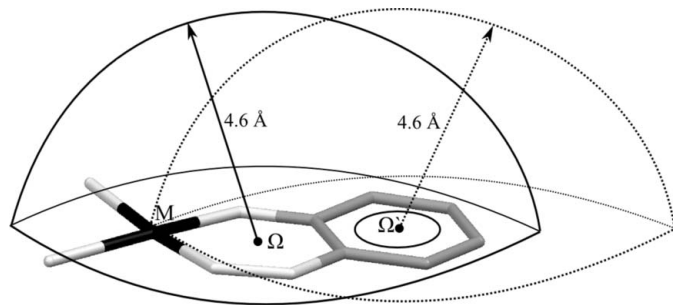


Figure 2
Schematic representation of the search method for intermolecular stacking interactions of the $C_{6\text{-arom}}$ ring with the chelate and the $C_{6\text{-arom}}$ ring. In the search distances between the $C_{6\text{-arom}}$ ring center of one complex to the chelate ring center (Ω), and also to the $C_{6\text{-arom}}$ ring center (Ω') of the other complex were restricted to be shorter than 4.6 \AA .

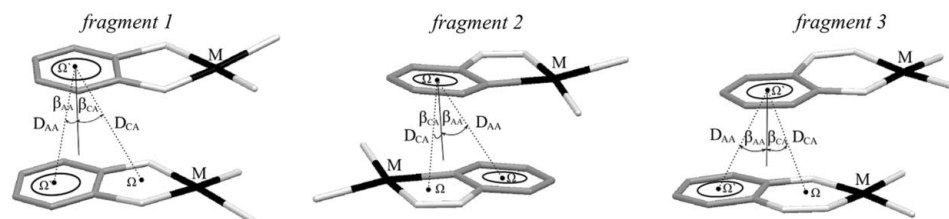


Figure 3
Schematic presentations of the intermolecular stacking interactions of square-planar fragments and parameters; D_{CA} is the distance between the centroids of the chelate and the $C_{6\text{-arom}}$ rings; β_{CA} is the angle between the normal to the $C_{6\text{-arom}}$ ring and the line that connect the centers of the chelate and $C_{6\text{-arom}}$ rings; D_{AA} is the distance between the centroids of two $C_{6\text{-arom}}$ rings; β_{AA} is the angle between the normal to the $C_{6\text{-arom}}$ ring and the line that connect the centers of two $C_{6\text{-arom}}$ rings.

Table 1
Constitution of chelate rings in fragments (Fig. 1) of square-planar complexes.

Fragment 1	Fragment 2	Fragment 3			
Ni(NCCN)	3	Pd(NCCC)	30	Ni(NCCCCO)	31
Ni(NCCS)	4	Pd(NNCC)	15	Ni(NCCCN)	1
Ni(NCCO)	2	Pd(OCCO)	2	Ni(NCCCS)	1
Pd(NCCN)	18	Pd(ONCC)	1	Ni(OCCCCO)	1
Pd(OCCO)	1	Pt(NCCC)	21	Pd(NCCCCO)	3
Pd(NCCS)	2	Pt(ONCC)	1	Pd(NNCCN)	1
Pd(SCCS)	1	Pt(NNCC)	2	Cu(NCCCCO)	37
Pd(NCCO)	8	Pt(NCCC)	1	Cu(OCCCCO)	1
Pd(NCCC)	7	Pt(NCCN)	1	Co(NCCCCO)	5
Pt(NCCS)	1	Au(NCCC)	15	Rh(OCCCCO)	2
Pt(NCCN)	12	Au(NNCC)	2	Pt(NCCCCO)	1
Pt(NCCC)	7	Ni(NCCC)	1	Rh(OCCNN)	1
Pt(PCCP)	1	Ni(POCC)	2		
Pt(OCCO)	1				
Pt(NCCO)	2				
Cu(NCCN)	18				
Cu(NCCO)	12				
Co(NCCN)	2				
Co(NCCS)	1				
Rh(NCCO)	2				
Au(SCCS)	1				

In these analysed crystal structures in most cases the Δ parameter has positive values. In complexes with all three fragments the peak distribution of the Δ parameter is in the region of $1.0\text{--}1.5 \text{ \AA}$ (Fig. 4). The fraction of interactions with positive values for Δ are: 70.6% for structures with the first fragment, 72.5% for structures with the second fragment and 75.5% for structures with the third fragment. These results show that in a large fraction of intermolecular interactions the $C_{6\text{-arom}}$ ring of one molecule is closer to the chelate than to the $C_{6\text{-arom}}$ ring of the other molecule.

The result indicating a possible preference of the $C_{6\text{-arom}}$ ring for stacking interactions with the chelate as opposed to the other $C_{6\text{-arom}}$ ring is in accordance with observations that the stacking interactions of organic heteroaromatic molecules with benzene are stronger than benzene–benzene stacking interactions (Hohenstein & Sherrill, 2009; Bates *et al.*, 2008; Ninković *et al.*, 2011, 2012). Calculations on the stacking interactions of benzene with the pyridine molecule reveal that the presence of a heteroatom will reduce the magnitude of the dispersion, induction and exchange–repulsion components of the interactions energies. The electrostatic term is very

important, significantly stabilizing and tends to dominate the interaction energy of stacking parallel-displaced configurations. It was pointed out that these general trends are observed for benzene–pyridine stacking and can be expected to persist in larger and more complex heteroatom-containing π systems (Hohenstein & Sherrill, 2009). Based on these results one can assume that the electrostatic component dominates in the preference of the $C_{6\text{-arom}}$ ring

for stacking interactions with chelate rings.

Square-planar complexes of each of the three fragments have various constitutions of chelate rings and contain various metal types. The constitutions of the chelate rings are given in Table 1. In order to examine the influence of metal type on stacking interactions the interactions were analysed separately for every metal type. The results are presented in Fig. 5. The results show that complexes of each metal type have a larger fraction of interactions with positive values of Δ , indicating a preference of the $C_{6\text{-arom}}$ ring to form stacking interactions with the chelate ring. This shows that the possible preference of the $C_{6\text{-arom}}$ ring to form stacking contacts with the chelate rings is ubiquitous and does not depend on the metal type.

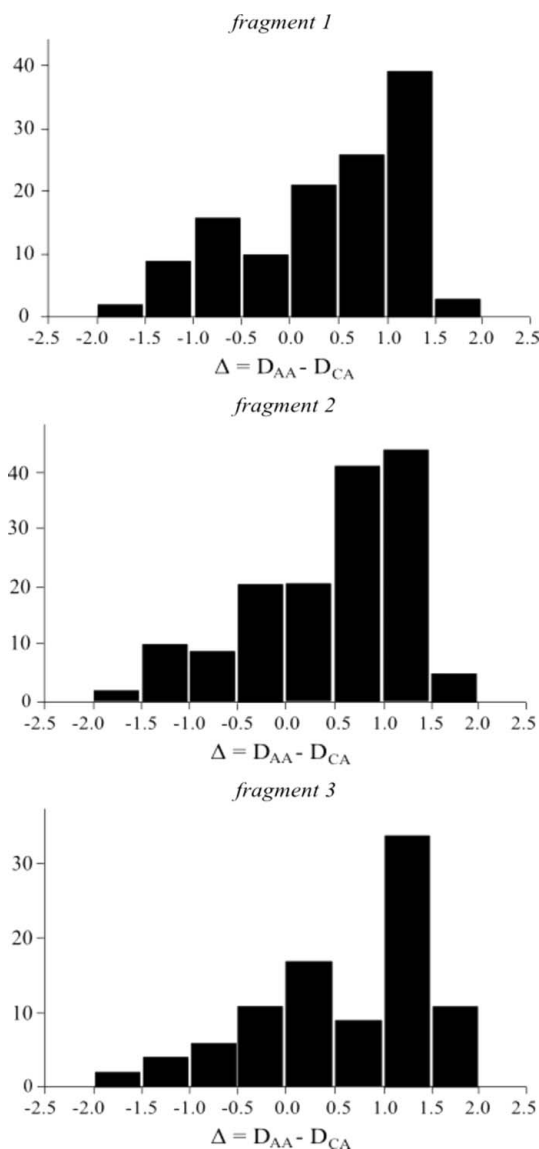


Figure 4
Histograms showing the distribution of Δ (Å) in crystal structures with five- (fragments 1 and 2) and six-membered (fragment 3) $C_{6\text{-arom}}$ -chelate fragments.

4. Conclusion

Analyses of the stacking interactions in the crystal structures of square-planar transition metal complexes with five- and six-membered chelate rings fused with $C_{6\text{-arom}}$ rings show a preference of the $C_{6\text{-arom}}$ ring for stacking interactions. The distribution of distances between the closest $C_{6\text{-arom}}-C_{6\text{-arom}}$

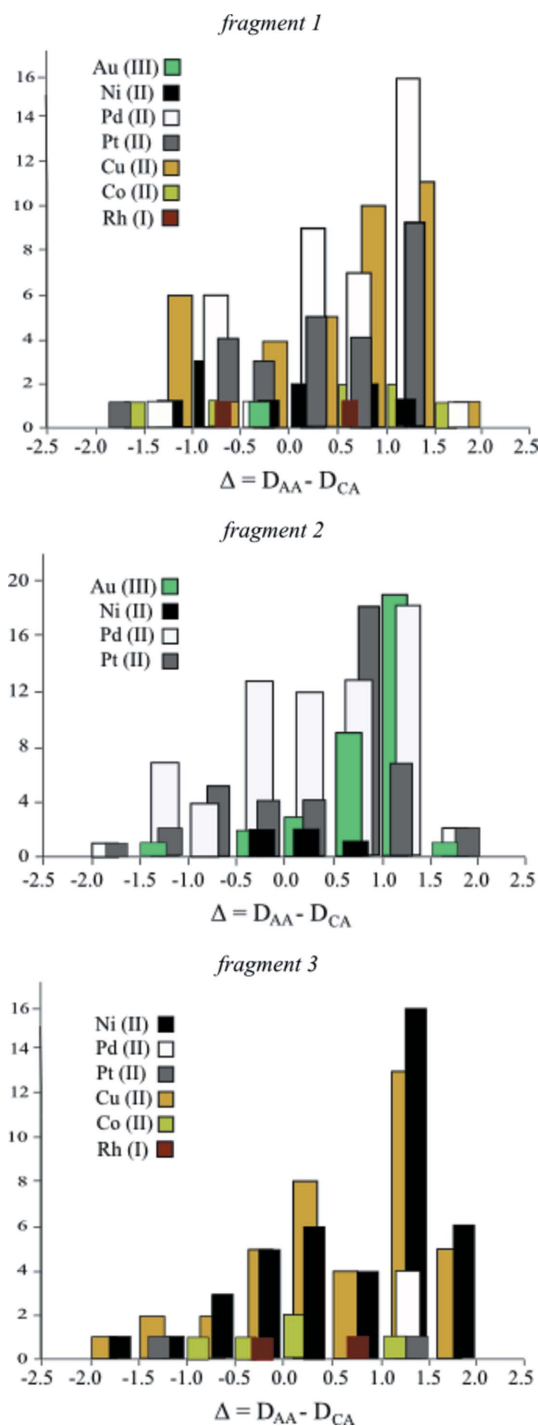


Figure 5
Histograms showing the distribution of Δ (Å) for various metal types in crystal structures with five- (fragments 1 and 2) and six-membered (fragment 3) $C_{6\text{-arom}}$ -chelate fragments.

and C_{6-*arom*}-chelate contacts shows that in a large fraction of the intermolecular interactions the C_{6-*arom*} ring of one molecule is closer to the chelate than to the C_{6-*arom*} ring of the other molecule. These results indicate a possible preference of the C_{6-*arom*} ring to form stacking contacts with the chelate rings. The preference is ubiquitous and does not depend on the metal type.

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