

## Influence of metal and ligand types on stacking interactions of phenyl rings with square-planar transition metal complexes

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**Abstract:** In order to find out whether metal type influences the stacking interactions of phenyl rings in square-planar complexes, geometrical parameters for Cu, Ni, Pd and Pt complexes, with and without chelate rings, were analyzed and compared. By searching the Cambridge Structural Database, 220 structures with Cu complexes, 211 with Ni complexes, 285 with Pd complexes, and 220 with Pt complexes were found. The results show that the chelate ring has a tendency to make the stacking interaction with the phenyl ring independent of metal type in the chelate ring. However, there are some differences among metals for complexes without a chelate ring. There are a number of structures containing Pd and Pt complexes, without chelate rings, that have short carbon-metal distances and parallel orientations of the phenyl ring with respect to the coordination plane. It was found that some of these complexes have a common fragment, CN, as a part of the ligands. This indicates that the CN supports stacking interactions of square planar complexes with the phenyl ring.

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## 1 Introduction

The importance of the noncovalent interactions of  $\pi$ -systems have been shown in different molecular systems from supramolecular structures to biomolecules [1–13]. In transition metal complexes there are specific types of noncovalent interactions of  $\pi$ -systems. Metal complexes, i.e. ligands coordinated to a metal, can interact with a  $\pi$ -system. In addition, interactions named metal-ligand-aromatic cation- $\pi$  interactions (MLAC $\pi$ ) [14–19], can be considered as a type of XH/ $\pi$  hydrogen bond [20–22]. It was shown that some of these interactions are among the strongest XH/ $\pi$  hydrogen bonds [18].

Recently, a few studies of noncovalent interactions with the  $\pi$ -system of chelate rings were published [18, 23–31]. The delocalized  $\pi$ -system of the chelate rings can be considered as a soft base, similar to double and triple bonds or aromatic rings, and could be connected with an assumption that planar chelate rings with delocalized  $\pi$ -bonds can have aromatic character [31]. The chelate ring can be involved in CH/ $\pi$  interactions with organic moieties and in stacking interactions with phenyl rings [18, 23–30].

Our previous results [26, 27] show that there are stacking interactions between the chelate and phenyl rings in square-planar complexes. These interactions were first recognized in square planar complexes of Cu [26]. Recently, the analysis of geometrical parameters in crystal structures of square planar complexes of all transition metals, from the Cambridge Structural Database, shows that there are stacking interactions between phenyl rings and chelate rings with delocalized  $\pi$ -bonds [27]. Short distances between the metal and carbon atom of the phenyl ring, and parallel orientations of the phenyl ring with respect to the coordination plane were found in crystal structures of complexes with chelate rings. There is a correlation between the metal-carbon distances and the distances between centers of the chelate and phenyl rings, indicating that the chelate and phenyl rings tend to overlap. In the crystal structures there are mutual slipped-parallel orientations of the phenyl and chelate rings [27], indicating that chelate rings can behave similar to organic aromatic rings.

In this work, in order to find out whether metal type has an influence on interactions of phenyl rings with square-planar complexes, geometrical parameters for Cu, Ni, Pd and Pt complexes, with and without chelate rings, were analyzed and compared. Moreover, in some cases influence of the ligands coordinated to a metal was analyzed.

## 2 Searching methods

The CSD search program Quest 3D [32] was used to retrieve structures satisfying the following criteria: (a) the crystallographic R factor  $\leq 10\%$ , (b) error-free coordinates according to the criteria used in the CSD system, (c) no crystallographic disorder, (d) no polymeric structures, (e) metal atom is coordinated by exactly four atoms according to the criteria used in the CSD system, (f) phenyl ring is present, (g) only one metal atom is present in the asymmetric unit. To ensure relative planarity of the complex molecule, the *trans* angles formed by the metal and coordinated atoms has been restricted to lie

between 150 and 180 °. To ensure planarity of the chelate ring we measured the torsion angles in the chelate ring and use only those with a maximum torsion angle value of less than 5 °. Geometrical parameters of the searched contact have been extracted by using the instructions implemented in program Quest, and additionally analyzed using the locally written programs. In the cases where more than one chelate ring is present in the molecule, we assume that the one whose centroid is closer to the centroid of the phenyl ring interacts with the phenyl ring.

### 3 Results and discussion

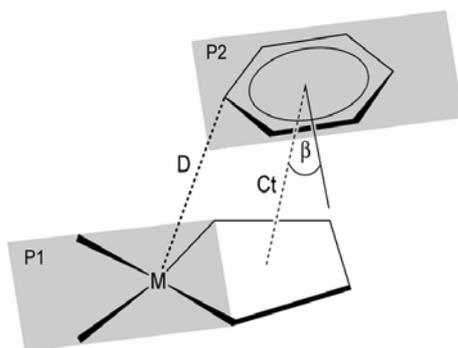
By searching the Cambridge Structural Database (CSD), using criteria described in the Searching Methods, 1124 structures with square-planar complexes and phenyl rings were found. Of these structures, 663 complexes contain a chelate ring. There are only four metal types (Cu, Ni, Pd, and Pt) with numbers of structures large enough to enable meaningful comparison of metal types. The large number of Cu, Ni, Pd and Pt containing structures is a consequence of the large tendency for these metals to form square-planar complexes. For Cu, Ni, Pd and Pt complexes, we found 220, 211, 285 and 220 structures, respectively. In most of the crystal structures metals are in the oxidation state +2, in only 18 structures there are metals in different oxidation states.

Crystal structures of Cu, Ni, Pd and Pt complexes, with and without chelate rings, were separately analyzed. Previous results showed that the presence of a chelate ring has an influence on the metal-phenyl carbon distance [26, 27]. Hence, we presented here histograms that show the distributions of number of structures with metal-carbon distance, i.e. parameter  $\Delta$  (Figure 2). The parameter  $\Delta$  is the difference of sum of the van der Waals radii and the distance between the metal and the closest phenyl carbon (D) (Figure 1) ( $\Delta = \Sigma \text{vdW} - D$ ). The parameter  $\Delta$  enables the use of criteria common for all metal atom types. Histograms are presented for the structures with (Figure 2a) and without chelate ring (Figure 2b).

The results show that complexes with chelate rings of all four metals have shorter metal-carbon distances, while complexes without chelate rings have longer metal-carbon distances (Figure 2). Hence, tendency of a chelate ring to make the stacking interaction with the phenyl ring is independent of the metal type in a chelate ring; however, there are some differences among metals (Figure 2). In the histograms for Cu, Pd and Pt complexes with chelate rings, the peaks of the distributions are in the regions with distances shorter than the sum of van der Waals radii ( $\Delta > 0$ ), while for Ni complexes the peak of the distribution is in the region with distances longer than the sum of van der Waals radii ( $\Delta < 0$ ). Nevertheless, the ratio of the number of structures with distances shorter ( $\Delta > 0$ ) and longer ( $\Delta < 0$ ) than sum of van der Waals radii is similar to the other metals.

The histograms for the complexes without chelate rings show some difference between Cu and Ni, on one side, and Pt and Pd complexes, on the other side. In cases of Cu and Ni complexes, the number of structures without chelate rings and short metal-carbon distances ( $\Delta > 0$ ) is very small, while in cases of Pt and Pd the percentage of these

structures is larger.

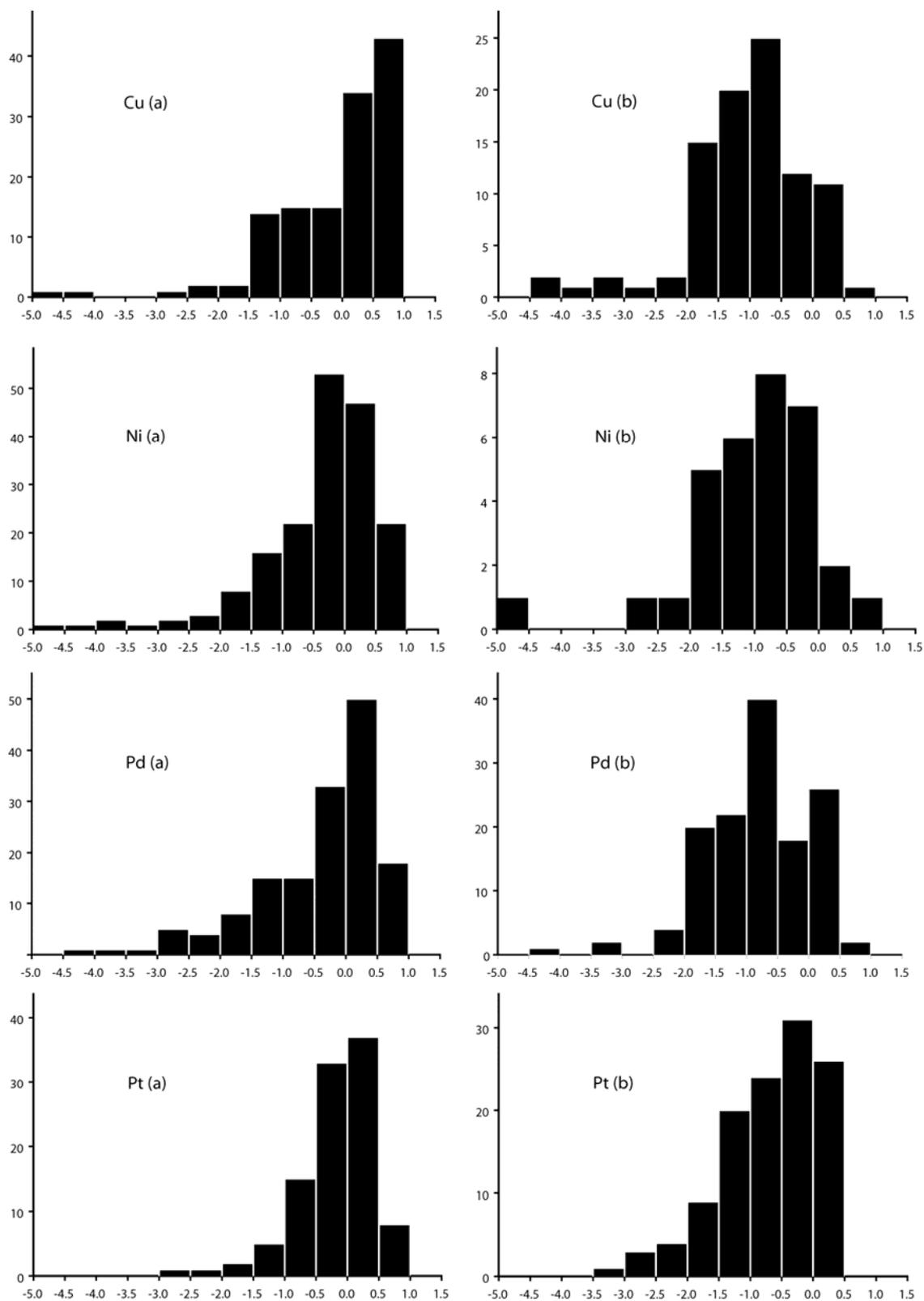


**Fig. 1** Geometrical parameters describing interaction of square-planar complex with phenyl ring.  $D$  is the distance between the metal and the closest phenyl carbon,  $Ct$  is the distance between the centers of chelate and phenyl ring,  $P1$  is the mean plane of metal and coordinated atoms,  $P2$  is the mean plane of phenyl ring,  $\beta$  is the angle between normal to phenyl ring and the line that connect the centers of chelate and phenyl rings.

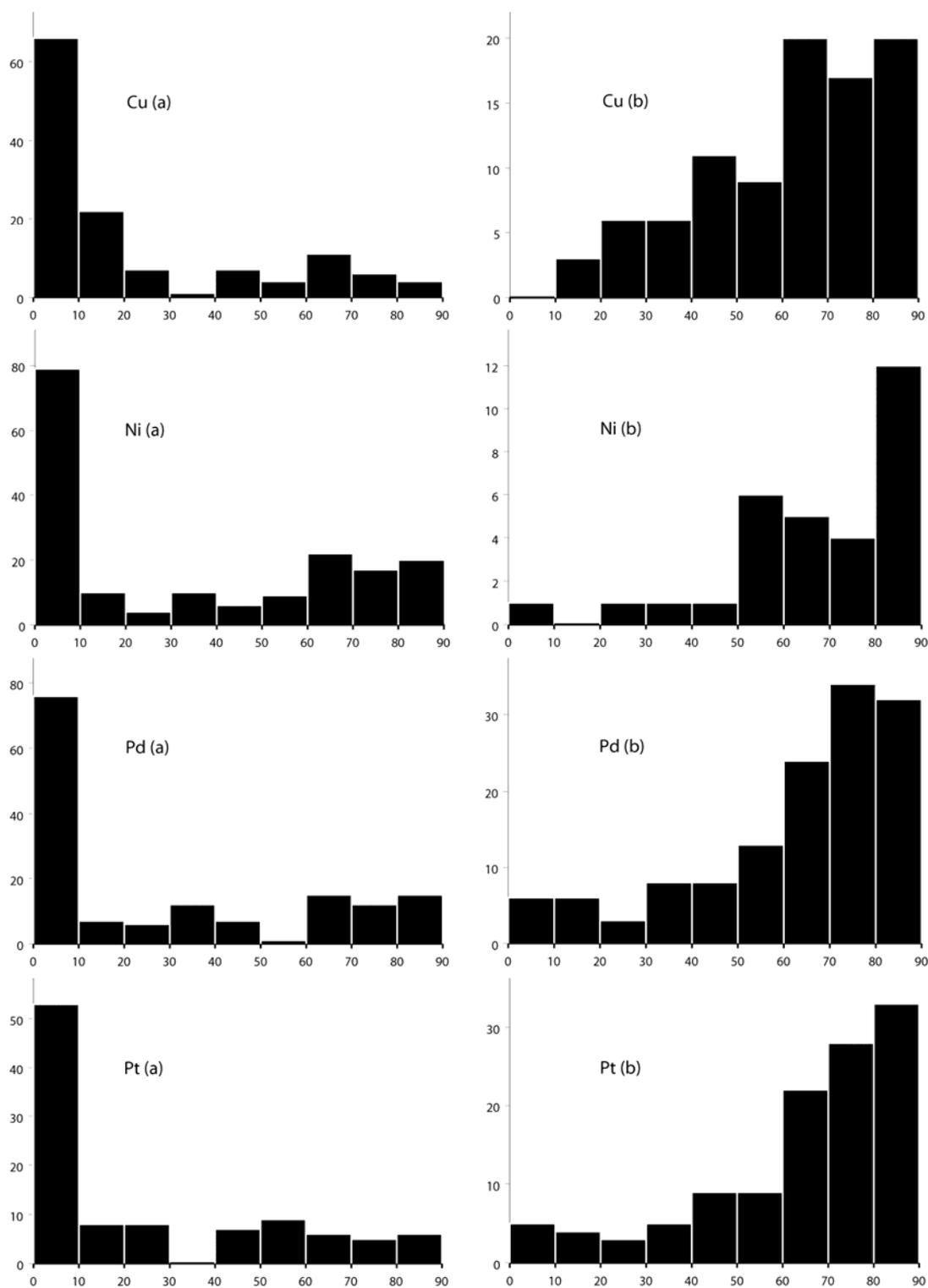
The other geometrical parameter important for stacking interactions is the dihedral angle  $\theta$ , i.e. the angle between the mean plane of the phenyl ring ( $P2$ ), and the mean coordination plane consisting of metal and coordinated atoms ( $P1$ ). The planes are shown in Figure 1. Distribution of this angle in structures with and without a chelate ring is shown in Figure 3, and data for all metals are similar to previously observed tendencies [27]. In the structures with a chelate ring, the phenyl ring has a large tendency to be oriented approximately parallel to the mean coordination plane (Figure 3a); in the structures without a chelate ring, the phenyl ring has a tendency to be oriented orthogonal to the coordination plane (Figure 3b). However, again there are some differences for structures without chelate rings among metals. While in Ni and Cu complexes there is a very small number of structures with  $\theta < 20^\circ$ , in cases of Pt and Pd there is a larger number of structures with  $\theta < 20^\circ$ . It is interesting to check if these structures of Pd and Pt, with a small angle  $\theta$ , also have short metal-carbon distances, indicating some kind of stacking interaction in complexes without a chelate ring.

We screened these complexes and found that in most cases when the dihedral angle is small ( $\theta < 20$ ) there are short metal-carbon distances ( $\Delta > 0$ ). Further analyses show that in many cases these complexes have common constitution of coordination sphere with coordinated cyano or isocyano phenyl derivatives (Figure 4). In some crystal structures the phenyl groups are oriented parallel to the mean coordination plane and lie above and below the metal atom, analogous to sandwich compounds (Figure 5).

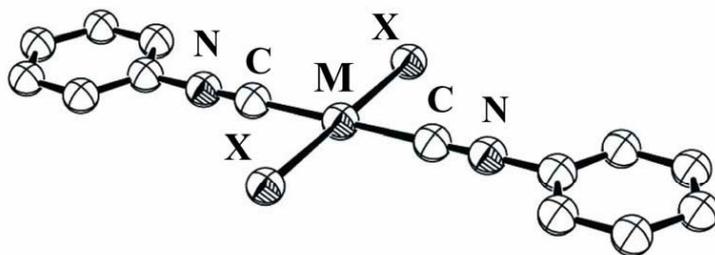
The histogram of distribution of dihedral angle  $\theta$  for Ni complexes without chelate rings (Figure 3, Ni (b)) shows that there is only one structure with  $\theta < 10$ . This is the crystal structure of complex with coordinated CN, similar to structures of Pd and Pt with small angle  $\theta$ .



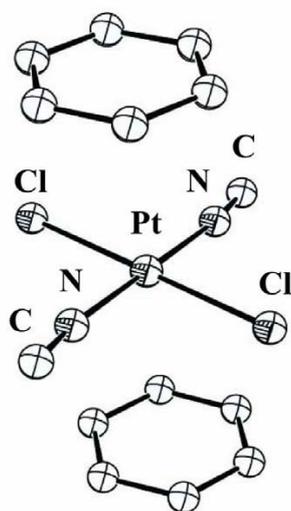
**Fig. 2** Histograms showing the distribution of parameter  $\Delta$  (Å) in crystal structure with (a) and without (b) chelate ring for Cu, Ni, Pd and Pt.



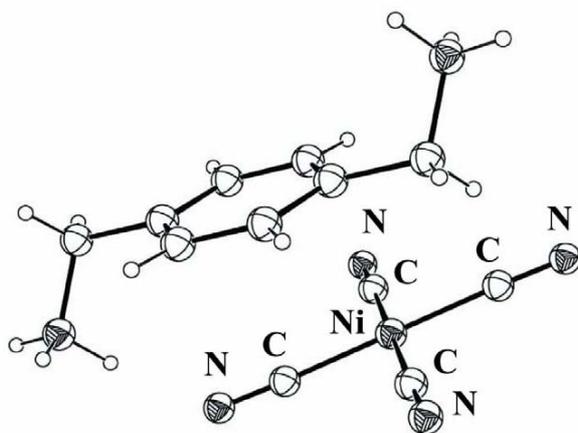
**Fig. 3** Histograms showing the distribution of the dihedral angle  $\theta$  ( $^{\circ}$ ) between the mean plane of the phenyl ring (P2) and the mean plane of the metal with coordinated atoms (P1) with (a) and without (b) chelate ring for Cu, Ni, Pd and Pt.



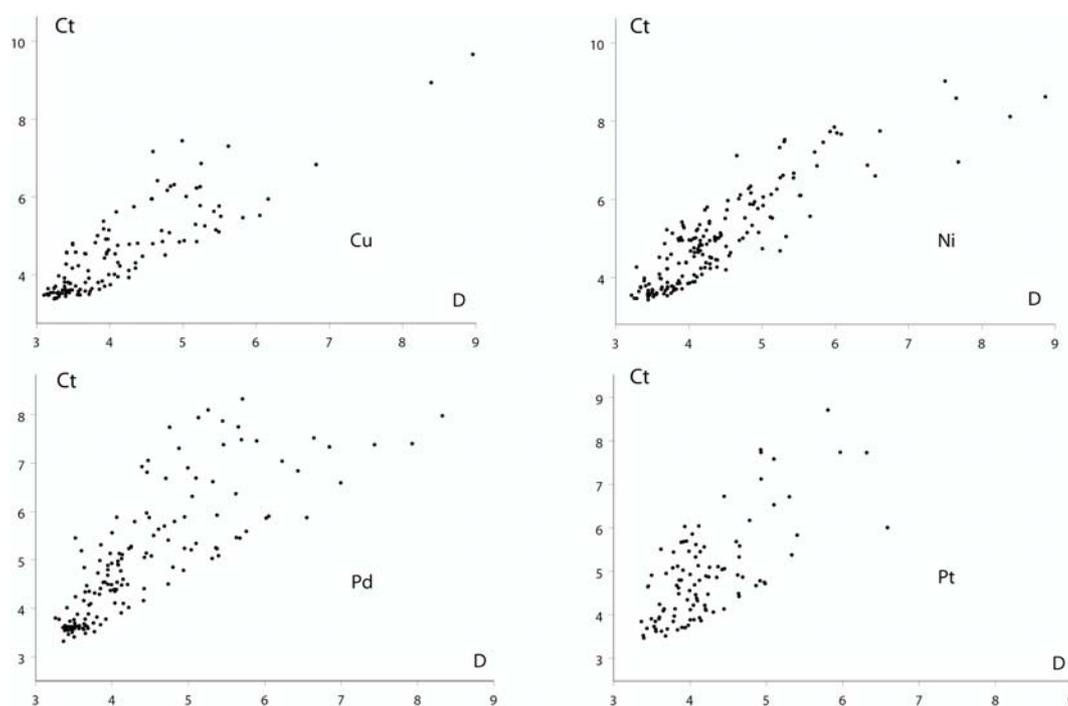
**Fig. 4** Common constitution for many complexes of Pd and Pt without chelate rings with small values of dihedral angle  $\theta$ , ( $X = \text{Cl, Br, I}$ ;  $M = \text{Pd, Pt}$ ). Part of crystal structure with refcode BOKREY ( $X = \text{I}$ ;  $M = \text{Pd}$ ).



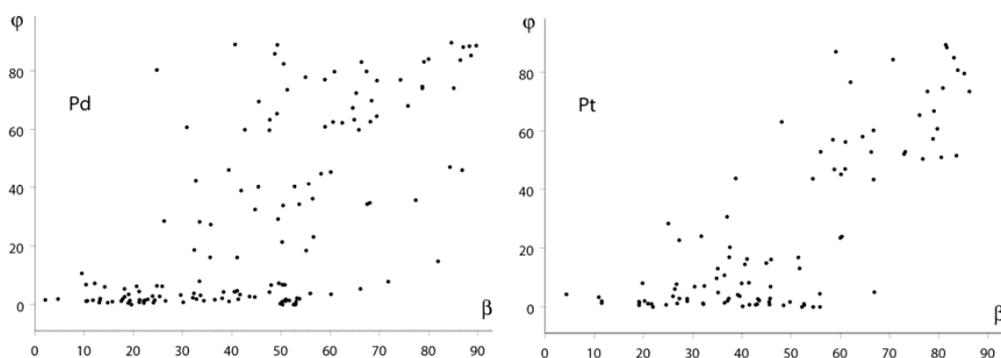
**Fig. 5** Part of crystal structures of refcode FUTHIL. Distance between Pt and center of phenyl ring is 3.549 Å.



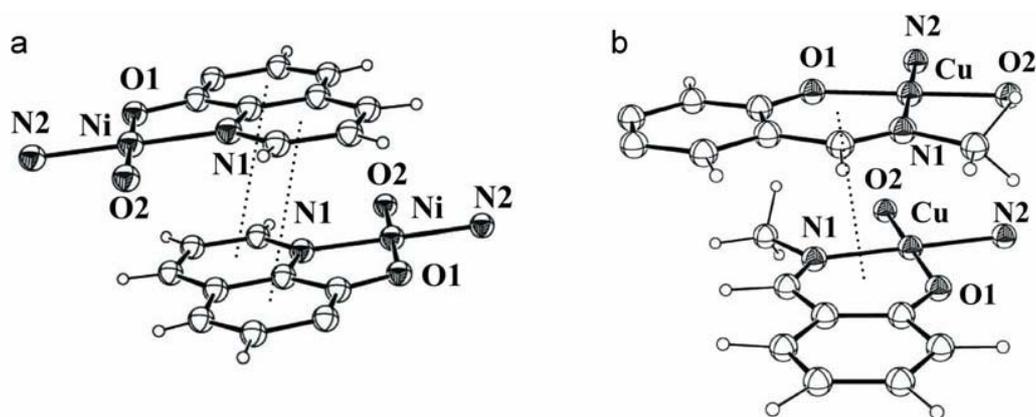
**Fig. 6** Crystal structure of refcode ZURRUZ.



**Fig. 7** Plot of the distances between the centers of the chelate and phenyl rings Ct ( $\text{\AA}$ ) versus the metal-carbon distance D ( $\text{\AA}$ ) for Cu, Ni, Pd and Pt.



**Fig. 8** Plot of the dihedral angle  $\varphi$  (angle between the mean planes of chelate and phenyl rings), versus angle  $\beta$  (angle between normal on phenyl ring and line connecting the centers of two rings (Figure 1)) for Pd and Pt.



**Fig. 9** Part of crystal structures of refcode **a.** JUHSUA **b.** MSACOP.

In the Ni complex the phenyl group of the *p*-xylene di-ammonium cation is oriented parallel to the mean plane of anion  $[\text{Ni}(\text{CN})_4]^{2-}$  (Figure 6). The examples Pd, Pt and Ni structures with CN and a small angle  $\theta$  show that the cyano fragment has a tendency to make stacking interactions with the phenyl ring, which is independent of the metal in the complex. The interactions of the phenyl ring and the complex are probably caused by  $\pi$  bonds in CN.

Previously it was shown [26, 27] that one of the consequences for the overlapping of two rings is correlation of distances between centers of the chelate and phenyl rings (Ct), and metal-carbon distances (D) (Figure 1). When the distance between centers of these two rings is shorter; the metal-carbon distance is also short. The plots for Cu, Ni, Pd and Pt are shown in Figure 7. All four have a similar pattern as previously reported [26, 27].

Positions of the phenyl rings with respect to chelate rings show that in all cases with a small dihedral angle  $\varphi$ , i.e. the angle between the mean planes of chelate and phenyl rings, the two rings are in mutual slipped-parallel orientations (offset face to face). The values of the dihedral angle  $\varphi$  plotted versus angle  $\beta$ , i.e. the angle between normal on phenyl ring and line connecting the centers of two rings (Figure 1), for Pd and Pt are shown in Figure 8. The plot shows that when the two rings are parallel (small dihedral angle  $\varphi$ ), angle  $\beta$  has, in most cases, values between 15 and 35°.

When the dihedral angle  $\varphi$  increases; the angle  $\beta$  increases too (Figure 8). However, for every metal there are structures with near parallel orientation of the two rings ( $\varphi \sim 0$ ) and larger values of angle  $\beta$  ( $\beta > 35$ ) (Figure 8). This means that the two rings are parallel but they do not overlap. We visually inspected these structures and found that in many cases the chelate ring is fused with other aromatic rings or a phenyl group. The parallel orientation is a result of the overlapping of two chelate rings or phenyl group and aromatic ring, which is condensed to a chelate ring (Figure 9).

## 4 Conclusion

The geometrical parameters describing stacking interactions of phenyl rings have been analyzed and compared for Cu, Ni, Pd and Pt complexes with and without chelate rings. The results show that complexes of all four metals with chelate rings have tendencies for shorter metal-carbon distances and parallel orientations of the phenyl ring with respect to the coordination plane. However, complexes without chelate rings favor longer metal-carbon distances and orthogonal orientations of the phenyl ring. Hence, the tendency for a chelate ring to make a stacking interaction with the phenyl ring is independent of metal type in the chelate ring. Analysis of other geometrical parameters supports this conclusion

However, there are some differences among metals for complexes without chelate rings. There are a number of structures containing Pd and Pt complexes without chelate rings that have short carbon-metal distances ( $\Delta > 0$ ) and parallel orientations of the phenyl ring with respect to the coordination plane. It was found that some of these complexes have a common fragment, CN, as a part of the ligands. This indicates that a CN supports stacking interactions of the phenyl ring with square planar complexes.

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