

STACKING INTERACTIONS BETWEEN PYRIDINE FRAGMENTS IN CRYSTAL STRUCTURES OF TERPYRIDYL COMPLEXES

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ABSTRACT. In the crystal structures of terpyridyl complexes from the Cambridge Structural Database (CSD) stacking interaction between the pyridine fragments were studied. Square-planar complexes where the distance between the centers of two pyridine fragments was below 4.6 Å were retrieved from CSD. With this search 68 crystal structures with 167 interactions were found. In the interactions one, two or three pyridine fragments of one complex can be involved in overlapping with pyridine fragments of the other complex.

Keywords: *Transition metal complexes, Crystal structures, stacking interaction, Cambridge Structural Database, terpyridyl*

INTRODUCTION

The noncovalent interactions of π -systems have been extensively studied in recent years. These interactions are important in many areas of chemistry and biochemistry [1–9]. The importance of noncovalent interactions of π -systems, cation– π [1–3], XH/ π hydrogen bonds (X = O,N,C) [4–7], and stacking interactions [4,8,9], have motivated studies of the noncovalent interactions in transition-metal complexes [10–14].

Several studies of chelate rings with delocalized π -bonds, which can be involved in noncovalent interactions [12–21] in ways similar to aromatic organic molecules [22], were published. Chelate rings can be involved in CH/ π interactions as hydrogen acceptors with organic moieties and in stacking interactions with aryl rings. The delocalized π -system of chelate rings can be considered as a soft base, similar to double, triple bonds or aromatic rings. These observations could be connected with an assumption that planar chelate rings with delocalized π -bonds can have aromatic character [23]. Several studies about interactions where the π -systems of chelate rings

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interact with C–H groups, belonging to an organic moiety, were published [15–18]. CH/ π interactions with chelate rings of coordinated porphyrin in transition metal porphyrinato complexes and in porphyrin containing proteins were also observed [16, 18]. The results showed that these interactions contribute to the stability of porphyrin containing proteins and may play some role in the function of these proteins [18].

We have analyzed CH/ π interactions between π -systems of coordinated acetylacetonato ligand and phenyl rings. Quantum chemical calculations on a few model systems show that the energies of the CH/ π interactions where the acetylacetonato ligand is the hydrogen atom donor (metal ligand CH/ π (MLCH/ π) interactions) are in the range of 0.6–2.4 kcal/mol, while the energies of the CH/ π interaction where phenyl group is the hydrogen atom donor are in the range of 1.5–2.7 kcal/mol [13].

Our previous results show that there are stacking interactions between chelate rings with delocalized π -bonds, and aryl rings containing six carbon atoms (C6-aryl), in crystal structures of square-planar transition-metal complexes [19, 20]. These interactions were first characterized in square-planar complexes of Cu(II). Further investigations show that interactions between chelate and phenyl rings exist in square-planar complexes of different transition metals. In these crystal structures, the geometry of the stacking interaction, between C6-aryl rings and chelate rings, is similar to the geometry of the stacking interaction of two benzene rings [22].

Here we present the results on stacking interactions between pyridine fragments in crystal structures of square planar terpyridyl complexes from the Cambridge Structural Database (CSD). We analyzed types of overlapping and mode of the packing in the crystal structures.

RESULTS AND DISCUSSION

A survey of crystal structures from CSD that contain square-planar terpyridyl complexes where the intermolecular distances between centroids of the two pyridine fragments are below 4.6 Å revealed 68 structures with 167 interactions. In order to describe these interactions, several geometrical parameters of the interactions were analyzed.

In Figure 1 a histogram presenting centroid-centroid distance (**D_{pp}**) of the two interacting pyridine fragments in the studied structures is shown. The distribution of the centroid-centroid distances has a peak from 3.6 to 3.9 Å, and for the substantial number of interactions the distance is above 4.0 Å.

The angle between planes P_1 and P_2 of the two pyridine fragments for almost all interactions is less than 10 degrees, indicating parallel or almost parallel orientation of the two rings. Normal distances (**R**) between the planes P_1 and P_2 are in the range of 3.0 to 3.8 Å, while the peak of the distribution is from 3.3 to 3.5 Å (Fig. 2). These normal distances are in agreement with the distances in stacking interactions [8a].

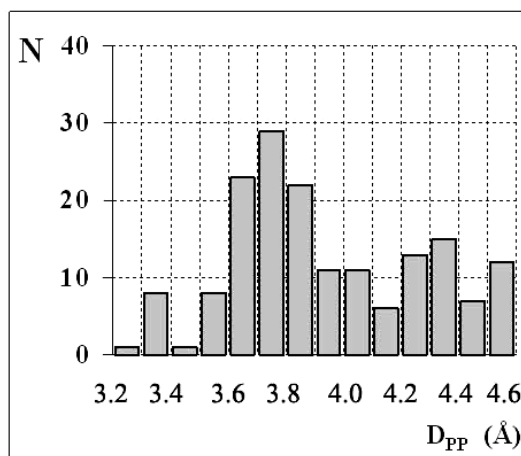


Figure 1. Histogram presenting centroid-centroid distance (**D_{pp}**) of the two interacting pyridine fragments.

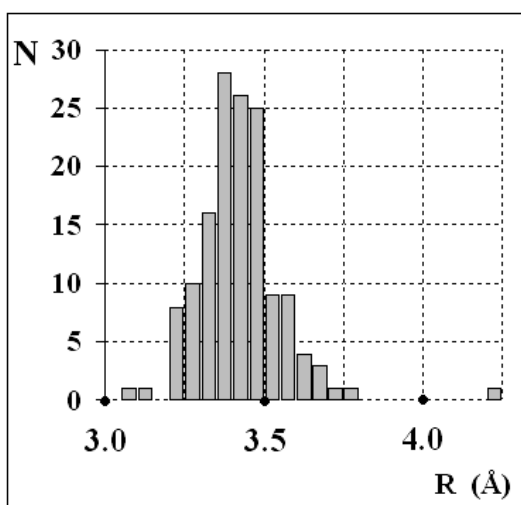


Figure 2. Histogram presenting normal distances (**R**) between the planes P_1 and P_2 of the two interacting pyridine fragments

The parallel orientations and normal distances of the pyridine fragments planes indicate the stacking interactions. In the terpyridyl ligand there are three pyridine fragments and there are possibilities that one, two or all three fragments are involved in the intermolecular stacking interactions. The analysis shows that only in three structures overlapping includes the whole ligand (and all three pyridine fragments) (Fig. 3). In these structures M...M distances are quite short. In the ABAXIL structure the metal ion is Ni^{2+} , and M...M distances

are 3.205, 3.142 and 3.204 Å. In the FECFOJ structure the metal ion is Ag^+ , with an M...M distance of 3.550 Å, while in the NEDVIC structure the metal ion is Pt^{2+} , with an M...M distance of 3.988 Å.

There are 9 interactions with very short Dpp distances, below 3.4 Å (Fig. 1). All these interactions are in ABAXIL structure where the two terpyridyl ligands of two complexes are overlapping with the whole surface.

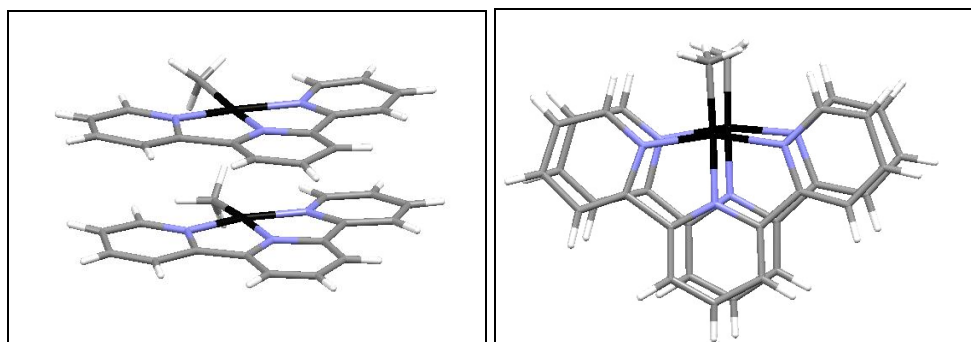


Figure 3. Overlap of square-planar complexes in crystal structure ABAXIL

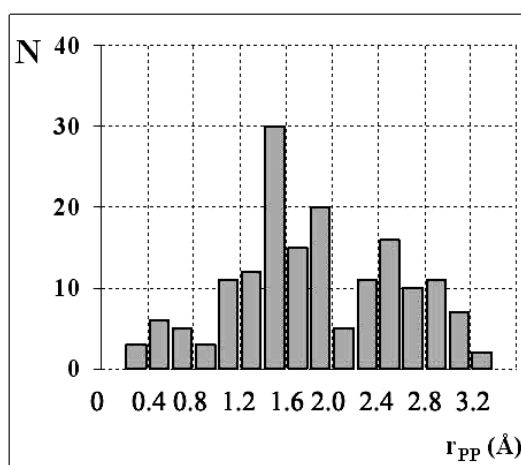
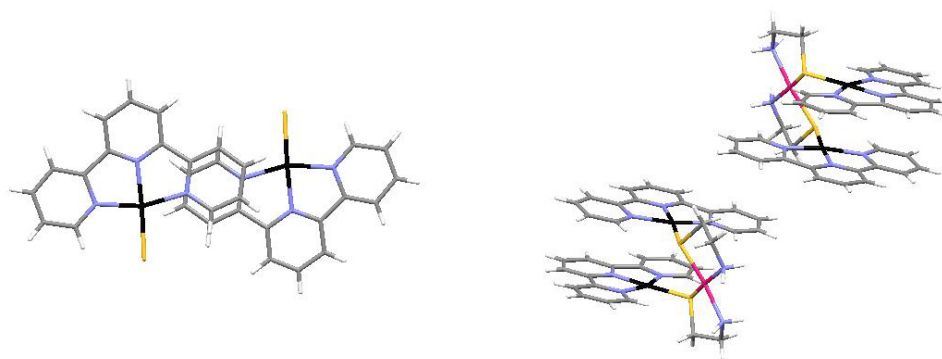


Figure 4. Histogram presenting horizontal displacement r of two interacting pyridine fragments

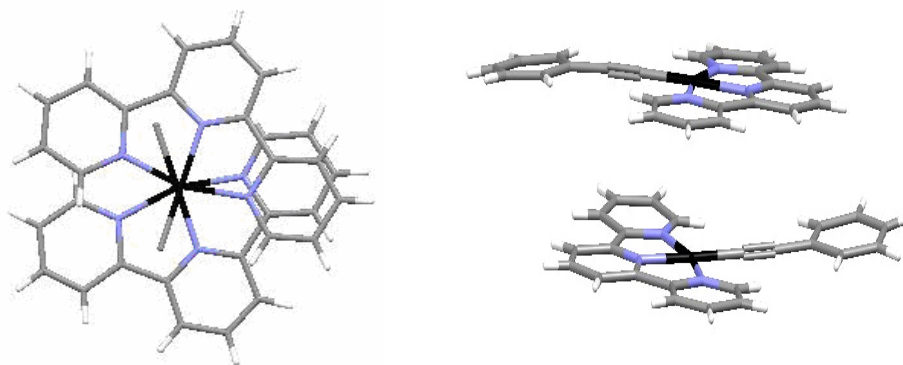
A histogram presenting the horizontal displacement r of two interacting pyridine fragments is shown in Fig. 4. In the ABAXIL structure there are very short **Dpp** distances, and also very short displacements r (Fig. 3). The other interactions with the displacement r smaller than 1.0 Å are in four structures where one ring overlaps and in two structures where two rings overlap. Two examples of structures where one ring is involved in overlap

are shown in Figure 5, structures GUMPUZ and PUWJIA. In both structures terminal pyridine fragments overlap, however, the orientations of the whole complexes are very different. In the structure PUWJIA metal-metal distance is very short (the Pt...Pt distance is 3.375 Å).

Two structures with overlap of two pyridine fragments are shown in Figure 6. In the structure LAJYUQ two terminal pyridine fragments overlap and so do both chelate rings; hence, a large part of the molecule is involved in the overlap, including also the metal atoms. In the structure NEVTAK, only the terminal and central pyridine fragment overlap, while the rest of the molecule is not involved in the overlap.

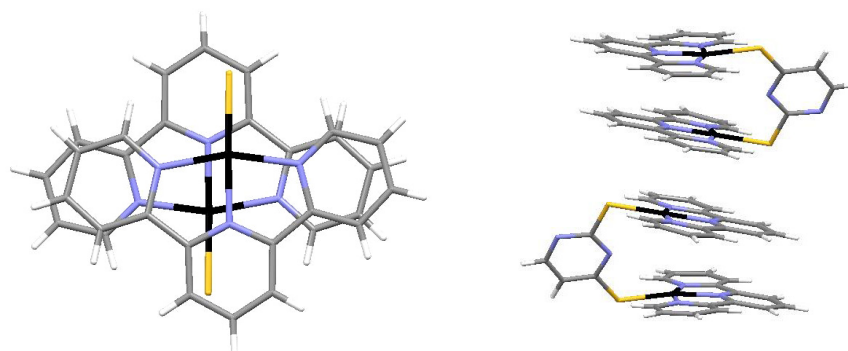


Structure GUMPUZ

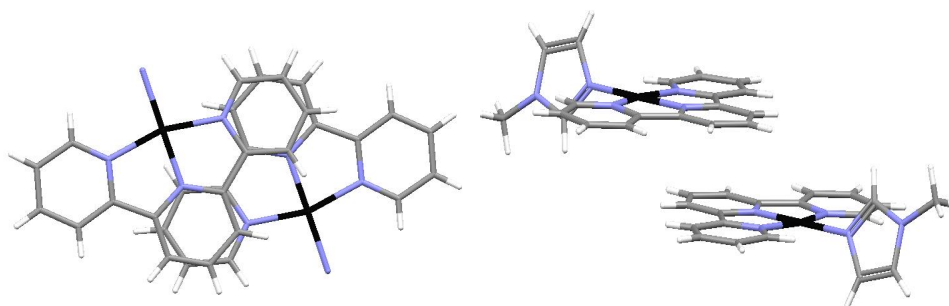


Structure PUWJIA

Figure 5. Overlap of terminal pyridine fragments in crystal structures GUMPUZ and PUWJIA



Structure LAJYUQ

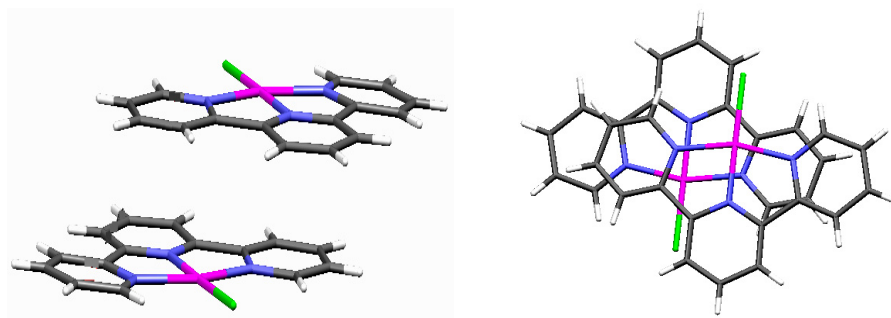


Structure NEVTAK

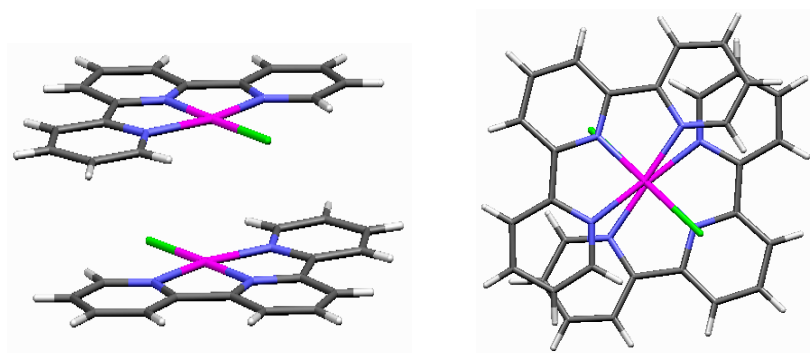
Figure 6. Overlapping of two pyridine fragments in crystal structures LAJYUQ and NEVTAK

The distribution of horizontal displacement r values shows that in large number for the structures r is from 1.4 to 2.0 Å (Fig. 4). However, a substantial number of structures have r value above 2.4 Å. When offset r is close to 3.0 Å, the overlap of the rings is quite small. The examples of the structures with the horizontal displacement r values in the range of 1.4 to 2.0 Å are given in the Fig. 7, 8, and 9.

In some of these structures, not only the pyridine fragment but also a large part of the complex is involved in the overlap (structures SASRUA01 and HAYNAX, Fig. 7). In these two structures the mutual orientations of the complexes are very different. In some complexes two pairs of pyridine fragments, terminal and central, can overlap, without involving the rest of the complex. The example is shown in Figure 8.



Structure SASRUA01



Structure HAYNAX

Figure 7. Example of the crystal structures in which large part of the complex is involved in the overlap

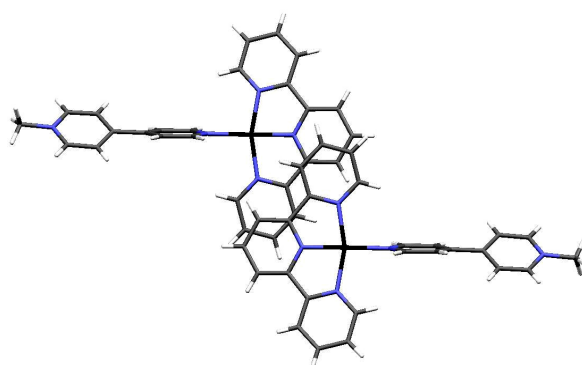


Figure 8. Example of crystal a structure (KAGQUF) with overlap of terminal and central pyridine fragments.

There are also examples where only one pyridine fragment is involved in the overlap. The example is structure NIKHIY with overlap of terminal pyridine fragments (Figure 9).

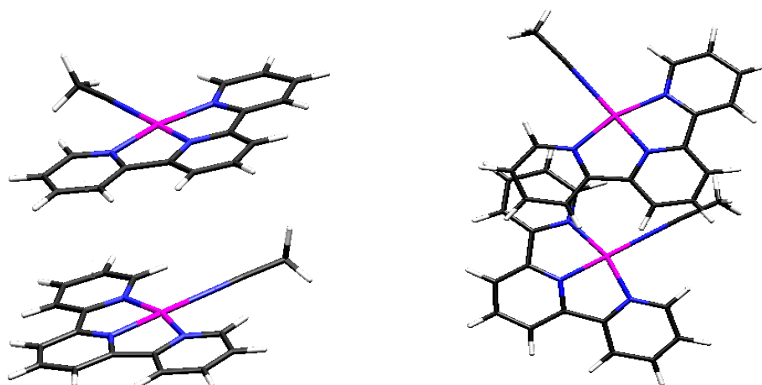
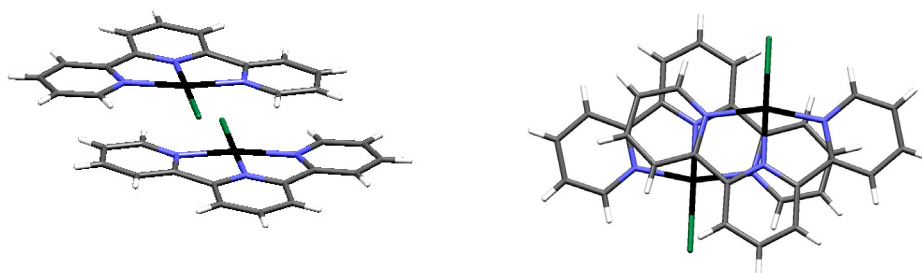


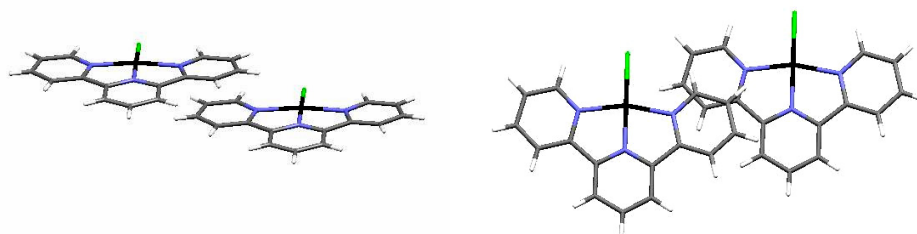
Figure 9. Overlap of terminal pyridine fragments in crystal structure NIKHIY

The examples of the structures with very small overlap area, and the horizontal displacement r larger of 2.5 Å are shown in Figures 10 and 11. The small overlap of pyridine fragments can occur in the structures where pyridine fragments overlap with chelate ring, structure AXEROK, Figure 10. Also small overlap can occur in structures where only terminal pyridine is involved, like in the structure BUYMOX.



Structure AXEROK

Figure 10. Example of the crystal structure with small overlap of pyridine fragments.



Structure BUYMOX

Figure 11. Example of the crystal structure with small overlap of pyridine fragments.

CONCLUSIONS

In the crystal structures of terpyridyl complexes from Cambridge Structural Database (CSD) stacking interactions between the pyridine fragments were studied. Square-planar complexes where the distance between the centers of two pyridine fragments was below 4.6 Å were retrieved from CSD. With this search 68 crystal structures with 167 interactions were found. In the interactions one, two or three pyridine fragments of one complex can be involved in overlapping with pyridine fragments of the other complex. The normal distances are in the range of 3.0 to 3.8 Å, in agreement with the typical distances in stacking interactions. The horizontal displacements of the two pyridine fragments are in large range, from values below 1.0 Å, up to 3.2 Å, indicating very different area of the overlap of the rings. In a small number of the structures whole area of the pyridine fragments overlap. In most of the structures the horizontal displacement is from 1.4 to 2.0 Å. Visual inspections of the structures revealed that various orientations of the pyridine fragments and the complexes are possible, with overlap of only one pyridine fragment of the complex, to overlap of the large area of the complex.

METHODOLOGY SECTION

The study is based on the crystal structures archived in the Cambridge Structural Database. The crystal structures of square-planar terpyridyl complexes were screened for intermolecular contacts. The CSD search program ConQuest 1.10 was used to retrieve structures satisfying the following criteria: a) the crystallographic R factor < 10% b) the error-free coordinates according to the

criteria used in the CSD c) the H-atom positions were normalized using the CSD default X-H bond lengths (O-H = 0.983 Å; C-H = 1.083 Å and N-H = 1.009 Å) d) no polymer structures.

In order to find intermolecular stacking interactions between terpyridyl ligands we searched for the structures with the distance between centroids of pyridine fragments below 4.6 Å. The same criteria were used before [8a]. This search separated 68 crystal structures with a total of 167 interactions. In the terpyridyl ligand there are two types of pyridine fragments: terminal (T) and central fragments (C) (Figure 12).

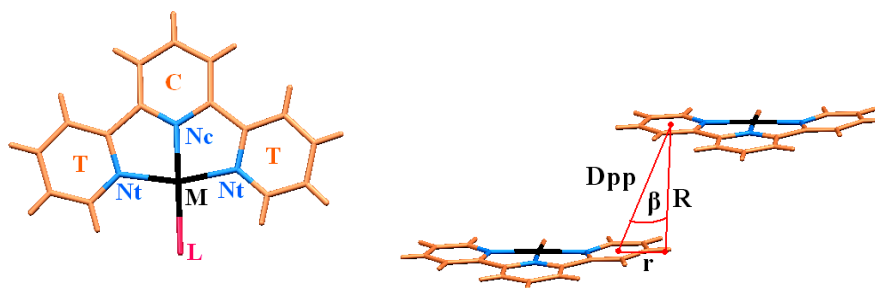


Figure 12. Atom labeling scheme and geometric parameters used for stacking interactions analysis

The geometric parameters used for analyzing geometries of the interactions and the atom labeling scheme are given in Figure 12. The distances between centroids of the rings are Dpp (two pyridine fragments). The angle β is defined as the angle between the vector connecting the centers of pyridine rings (Dpp) and the normal to the plane of one of the rings. The normal distance between the planes of interacting rings is R. The distance of the projection of the center of the first pyridine ring onto the plane of the second ring from the center of the second ring is the horizontal displacement r (Figure 12).

T₁

T₂

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