

Geometries of stacking interactions between phenanthroline ligands in crystal structures of square-planar metal complexes

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Abstract Stacking interactions of phenanthroline square-planar complexes in crystal structures were studied by analyzing data from the Cambridge Structural Database. In most of the crystal structures, two phenanthroline complexes were oriented “head to tail.” Phenanthroline complexes show a wide range of overlap geometries in stacking interactions, while short metal–metal distances were not observed. Stacking chains with alternating overlaps were the predominant type of packing in the crystal structures.

Keywords Stacking interactions · Cambridge Structural Database · Aromatic · Metal complexes

Introduction

The characterization of stacking interactions is a challenge both experimentally and theoretically. Recently, several new methods have been developed and used intensively to study stacking interactions [1–10]. Stacking interactions between aromatic organic molecules or fragments are generally studied. However, it was shown that other planar molecules and fragments can be also involved in stacking interactions [11–24]. Several studies of chelate rings with

delocalized π -bonds, which can be involved in similar stacking interactions [11–21] to aromatic organic molecules [6–8], were published.

Stacking interactions between chelate and C_6 -aromatic rings were identified by analyzing the data on the crystal structures of square-planar transition metal complexes from the Cambridge Structural Database (CSD) [11, 12, 14]. In the crystal structures, the rings have a mutual slipped-parallel orientation, similar to that of two benzene rings [6–8]. Chelate rings can be also involved (as hydrogen acceptors) in CH/ π interactions with organic moieties [25–33]. Comparison of stacking vs. CH/ π interactions of C_6 -aromatic rings with chelate rings in crystal structures of square-planar complexes showed that the stacking interactions are preferred to CH/ π interactions [21]. Recently, we showed the existence of chelate–chelate stacking interactions in crystal structures from the CSD [34]. Chelate–chelate stacking interactions occur in a large number of crystal structures. The normal distances associated with such interactions are similar to those of stacking interactions observed in other systems, while the offset of two interacting chelate rings can differ from that observed in the other systems.

A geometrical analysis of stacking interactions with aromatic nitrogen-containing ligands, based on the CSD [35], showed that nitrogen-containing aromatic rings usually adopt a slipped π – π alignment where most of the ring-plane area overlaps.

We recently studied stacking interactions of terpyridyl square-planar complexes in crystal structures by analyzing the data from the CSD [36]. In most of the crystal structures, two terpyridyl complexes were oriented “head to tail” or “head to head,” with the head-to-tail orientation prevalent. The number of structures with other orientations was very small. Based on the analysis of interacting

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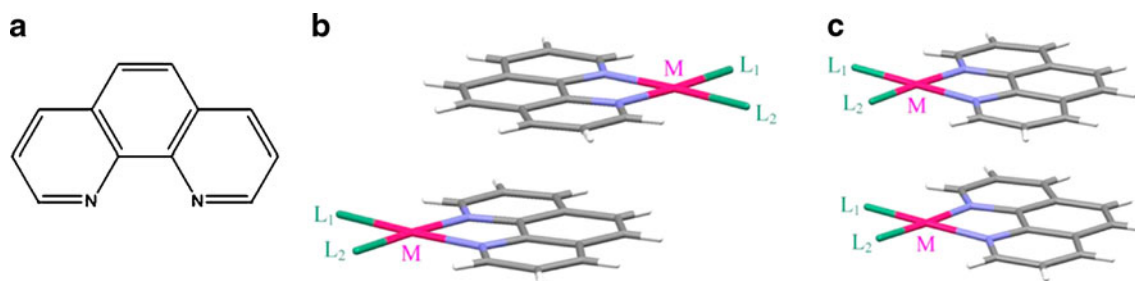


Fig. 1 a ChemDraw structure of the phenanthroline molecule, and schematic diagrams of b “head-to-tail” and c “head-to-head” orientations

geometries, we classified overlaps of terpyridyl complexes into six types. The types were defined by values of several geometrical parameters, and all interactions of the same type had very similar overlap patterns.

Similar to the terpyridyl ligand, the phenanthroline (1,10-phenanthroline-*N,N'*; Fig. 1) molecule coordinating to a metal ion forms a large planar system of four rings: two pyridine fragments, one C_6 -ring, and one chelate ring. This planar system has a propensity to form stacking interactions with the π -systems of various aromatic groups. Some papers present interesting properties of phenanthroline complexes that are used in a number of devices from photoactive devices [37] to antitumor agents [38]. The tendency for stacking interactions to occur is an important issue when using these complexes in various fields. For example, it is known that phenanthroline complexes interact with DNA by intercalating between base pairs of DNA [39].

To better understand stacking interactions of phenanthroline complexes, here we analyze the geometry of stacking interactions between phenanthroline square-planar metal complexes in crystal structures from the CSD.

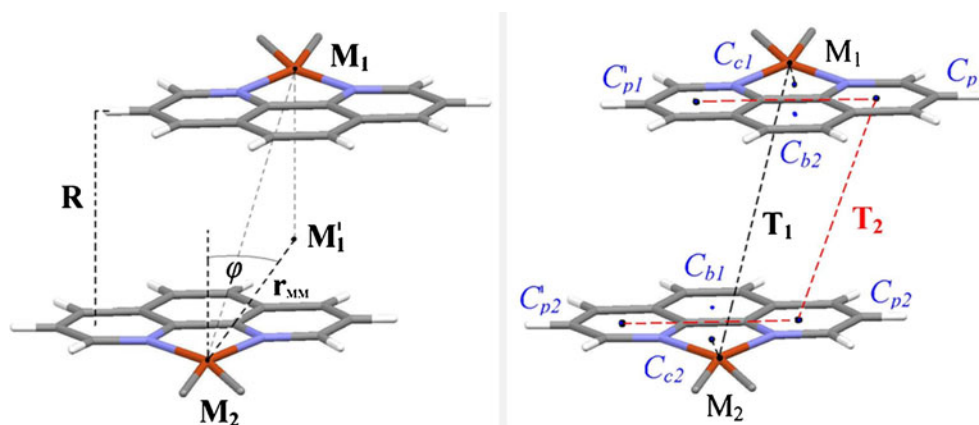
Searching methods

In order to find intermolecular stacking interactions between phenanthroline (phen) complexes, we used the same criterion that has been used before in a study of

stacking interactions of aromatic nitrogen-containing ligands where the distance between centroids of the rings was below 4.6 Å [35]. The study was based on the crystal structures archived in the Cambridge Structural Database (November 2009 release, version 5.31 [40]). Crystal structures involving phen complexes with a coordination number of 4 were screened for intermolecular contacts. The CSD search program ConQuest 1.10 [41] was used to retrieve structures satisfying the following criteria: (a) error-free coordinates were available (according to the criteria used in the CSD); (b) the crystallographic R factor <10%; (c) no polymer structures; (d) the H-atom positions were normalized using the CSD default X–H bond lengths (O–H=0.983 Å; C–H=1.083 Å; N–H = 1.009 Å) [42].

The coordinated phen ligand has four fused rings: two pyridine fragments, one C_6 -ring and one chelate ring (Fig. 2). Since we have shown that chelate rings can also form stacking interactions [11–14], we searched for the distances between the centroid of any ring of the phen ligand in one complex and the centroid of any ring in the other complex: d_{pp} , d_{bb} , d_{cc} , d_{pb} , d_{pc} , d_{bc} . Distances d_{pp} , d_{bb} , and d_{cc} are the intermolecular distances between the centroids of two pyridine fragments, two C_6 -rings, and two chelate rings, respectively. Distance d_{pb} is the distance between the centroids of pyridine and C_6 -rings, d_{pc} is the distance between the centroids of pyridine and chelate rings, and d_{bc} is the distance between the centroids of C_6 and chelate rings (Fig. 2).

Fig. 2 Geometrical parameters describing interactions



The geometric parameters used to analyze the stacking interactions of phen ligands are presented in Fig. 2. The normal distance between the planes of the interacting rings is R . In Fig. 2, the center of a chelate ring is shown as C_h , the center of a C_6 -ring as C_b , while the center of a pyridine ring is marked as C_p . The distance between the metal ion of the second complex (M_2) and the projection of the metal ion of the first complex (M_1) onto the average plane of the second one (M'_1) represents the horizontal displacement r_{MM} . The angle between the $M_1M'_2$ and M_1Ch_1 directions in the plane of the second complex is denoted φ .

Two torsion angles T_1 and T_2 are shown in Fig. 2b. Torsion angle T_1 is the $Ch_1M_1M_2Ch_2$ angle. Torsion angle T_2 is the $Cp_1'Cp_1Cp_2Cp_2'$ angle, where Cp_1 and Cp_2 are the centroids of the pyridine rings in the two complexes that are the closest together.

Results and discussion

By searching the Cambridge Structural Database (CSD) using the criterion that the intermolecular distances between centroids of any of the rings must be below 4.6 Å, as described in the “Searching methods” section, 81 structures with 172 stacking interactions between phen square-planar complexes were found. Using this criterion, in most of the interactions (168) the contact planes of the phen ligands were parallel; the dihedral angle between the planes was less than 10°. We used these 168 interactions with parallel contact planes for our subsequent analysis.

The mutual orientations of the interacting complexes were analyzed using the geometrical parameters shown in Fig. 2. The distribution of the normal distances between the interacting pyridine fragments shows a peak at 3.3–3.5 Å, while in a large number of interactions the normal distances are in the region of 3.2–3.7 Å (Fig. 3). These normal

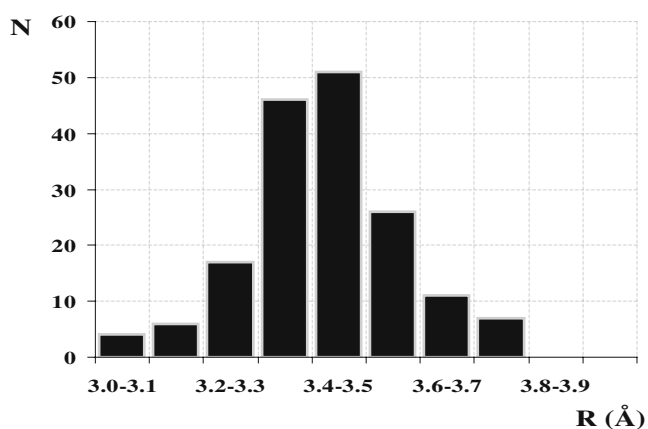


Fig. 3 Histogram of the distribution of the normal distance R between interacting pyridine fragments in square-planar phen complexes

distances are typical of stacking interactions [35]. A similar distribution of normal distances was observed for stacking interactions of terpy complexes [36].

The distribution of T_1 torsion angle values (Fig. 2) shows preferred orientations with angles of 170–180° (head-to-tail orientation) (Fig. 4). The number of interactions with angles of 0–10° (head-to-head orientation) is quite small (only 10 interactions). Also, the number of interactions with $T_1 = 10$ –170° is very small. In our previous work on stacking interactions of square-planar terpy complexes, we found a preference for a head-to-tail orientation; however, the fraction of interactions with a head-to-head orientation was quite large [36]. Since both terpy and phen ligands coordinated to a metal form planar delocalized systems, the explanation for the larger number of head-to-head orientations of terpy complexes may be connected with the other ligands in the complex. Our previous results on terpy complexes showed an important influence of the second ligand (occupying the fourth coordination position) on the stacking interaction [36]. When the fourth ligand was large, head-to-head orientations were prevented. In square-planar complexes, the terpy ligand occupies three coordination positions, while the phen ligand occupies two coordination positions. Therefore, in phen complexes, there are two other ligands in the complex, and their influence leads to a reduced probability of head-to-head orientations.

The distribution of the T_2 torsion angle (Fig. 2) shows two preferred orientations; the first has T_2 values of 0–10°, and the second has values of 170–180° (Fig. 4). A small number of the interactions have T_2 angles of 10–170°. T_2 torsion angles of 0–10° correspond to interactions that involve the overlap of a large part of the phen ligands, while values of 170–180° correspond to interactions that involve only partial overlap of the phen ligands. Interactions with values of T_2 in the range 0–10° are encountered more often. We obtained similar results for terpy complexes, although orientations with T_2 values of 170–180° were rather more frequent [36].

Because of the preferences for one particular value of the torsion angle T_1 and the two values of T_2 , two possible combinations of these torsion angles can describe most of the intermolecular stacking interactions of phen square-planar complexes. The values of T_1 are close to 180°, so complexes are oriented head to tail, while T_2 values can be close to 0° (group I) or close to 180° (group II).

The mutual displacement of the two interacting phen complexes was measured by two parameters: the angle φ and the offset r_{MM} (Fig. 2). In our previous work, we showed that these two parameters were important for describing the mutual orientations of terpy complexes [36]. The scattergram for the correlation between φ and r_{MM} for phen complexes is shown in Fig. 5, for both groups

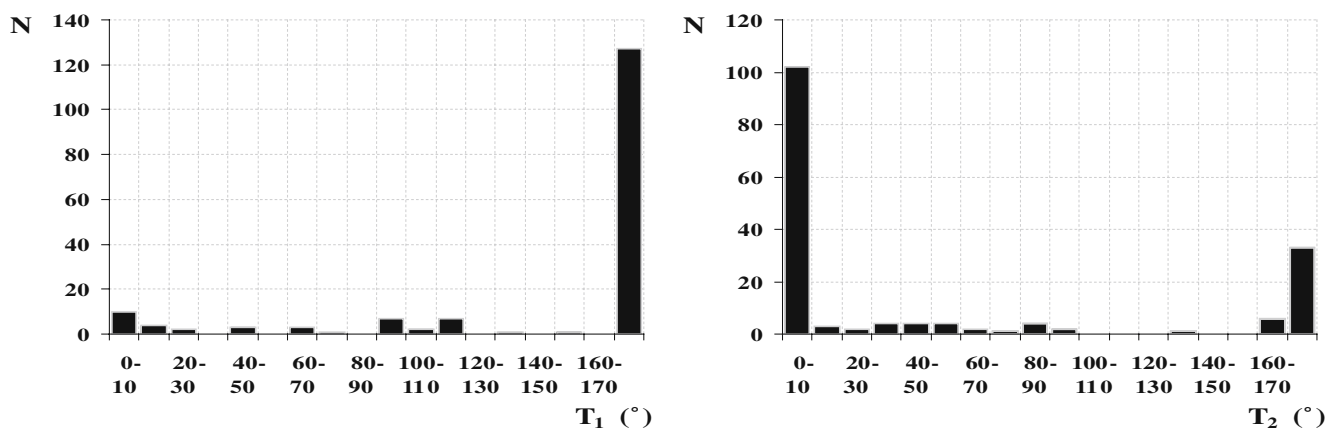


Fig. 4 Histograms showing the distributions of the torsion angles T_1 and T_2 for interactions of square-planar phen complexes

(I and II). The interactions of the two groups differ in the angle φ ; the interactions of group I have quite small values of φ (below 20°), while the interactions of group II have larger values of φ (mainly above 20° , although with several exceptions, and up to 70°). Both groups show a large range of r_{MM} values, but the values are lower for group I. The values of r_{MM} for group I range from 3 to 10 Å, while those for group II range from 4 to 11 Å.

The ranges of φ and r_{MM} are quite different for the stacking interactions of terpy complexes [36], indicating that these complexes have different overlaps compared to the phen complexes. For the interactions of terpy complexes, φ values are larger, in the range of 20 – 140° . However, for the terpy complexes, the r_{MM} values are smaller—ranging from 0 to 10 Å—indicating short metal–metal interactions. These short metal–metal distances were not observed in stacking interactions of phen complexes. On the other hand, the smaller values of the angle φ indicate that in the phen complexes there is greater overlap than in terpy complexes. This greater overlap can be observed in the examples of the interactions in the crystal structures

presented in the figures in our previous paper [36], and here.

Another very important difference between stacking interactions of terpy and phen complexes is the potential degree of classification of the interactions. We showed that for the terpy complexes it was possible to classify the interactions into six types based on the clustering in the scattergram of φ vs. r_{MM} (Fig. 4 in [36]). All interactions of the same type were clustered together on the scattergram and showed very similar overlap patterns. The scattergram in Fig. 5 does not show clustering. Hence, we can only talk about two groups of interactions based on the values of T_2 , as explained above. Visual inspection indicates that interactions in the same group can be quite different, as also indicated by the wide range of r_{MM} values observed in each group. Thus, there are several types of overlap for each group.

Group I, with T_2 values that are close to 0° , is the larger of the two groups: it includes 45 structures with 93 interactions. For this group, φ values are less than 20° and values of r_{MM} are in the range 3.0–10.0 Å (mean value is 6.67 Å). The distribution of r_{MM} presented in Fig. 6 shows

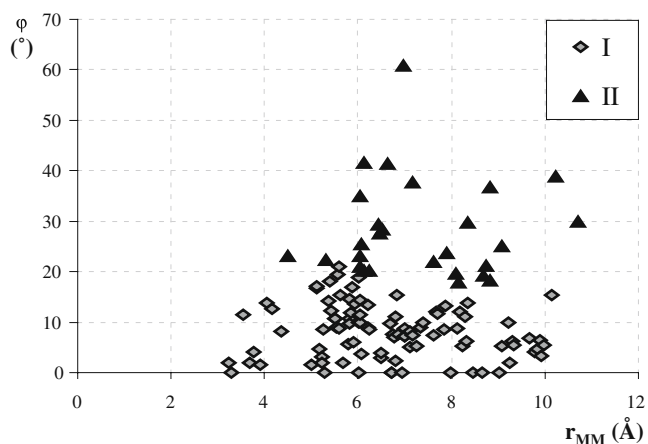


Fig. 5 Scattergram for the correlation between φ and r_{MM} for group I and group II phen complexes

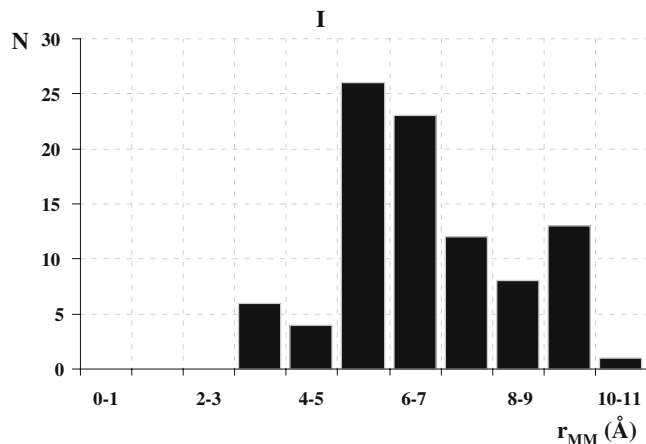


Fig. 6 Histogram of the distribution of r_{MM} values for group I interactions

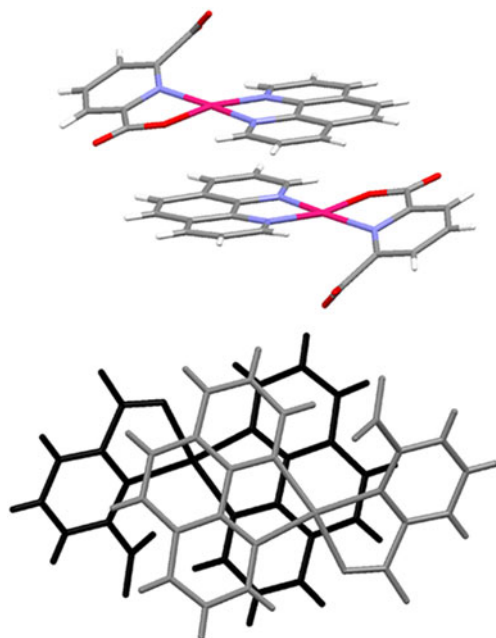


Fig. 7 Two projections presenting the stacking interactions in the CAQTEU crystal structure [43], i.e., (1,10-phenanthroline-*N,N'*)-(2,6-pyridinedicarboxylato-*N,O*)-palladium(II) tetrahydrate, as an example of a group I interaction with small value of r_{MM} (3.53 Å, $\varphi=11.5^\circ$)

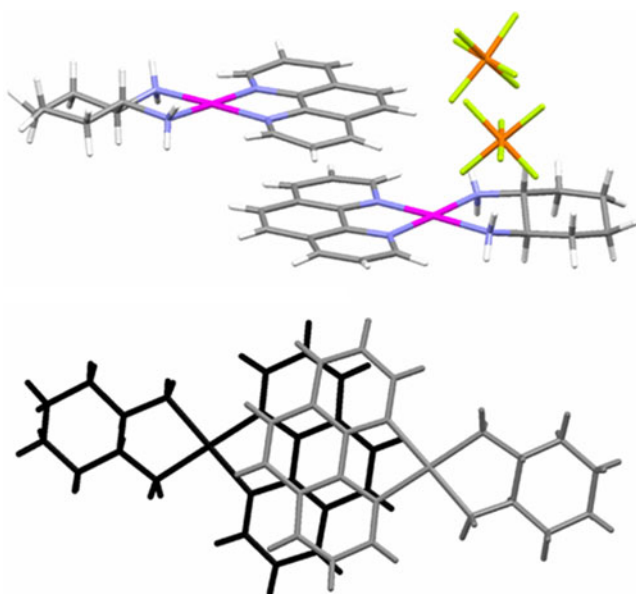


Fig. 8 Two projections presenting the stacking interactions in the BEBCAN crystal structure [44], i.e., ((1*R*,2*R*)-1,2-diaminocyclohexane-*N,N'*)-(1,10-phenanthroline-*N,N'*)-platinum(II) bis(hexafluorophosphate), as an example of a group I interaction with mutually overlapping C_6 -rings. The phenanthroline ligand interacts with the ion from the external sphere of the complex ($r_{MM}=6.86$ Å and $\varphi=7.5^\circ$)

a peak at 5.0–6.0 Å, while it is in the interval 5.0–8.0 Å for a large number of the interactions. By visually inspecting the interactions, we found that there are mutual overlaps between both pyridine rings in most of the interactions.

Structures with small values of r_{MM} are associated with chelate–chelate, chelate– C_6 -ring, and mutual overlaps of pyridine rings (Fig. 7). Mutual overlaps of C_6 -rings do not occur. Chelate– C_6 -ring overlap involves a large area of overlap with the C_6 -ring, while chelate–chelate overlap is small. In addition, in these structures the metal ion is mainly located above the C_6 -ring, as suggested by the values of φ and r_{MM} . This overlap is possible because the other two ligands are not voluminous. This point is illustrated in Fig. 7, which represents the CAQTEU crystal structure [43]. In this structure, the metal ion is Pd^{2+} , and the distance between the metal ion and the center of the C_6 -ring is 3.67 Å, indicating that there is an interaction between the metal ion and the π -system of the C_6 -ring.

A large number of interactions (61) occur in the r_{MM} region of 5.0–8.0 Å. In these structures, there are mutual overlaps of pyridine fragments, mutual overlaps of C_6 -rings,

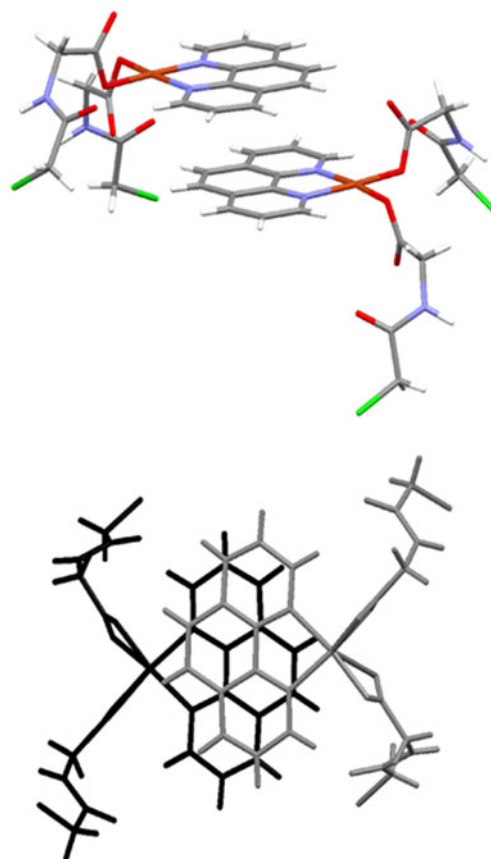


Fig. 9 Two projections presenting stacking interactions in the NOBYOS crystal structure [45], i.e., bis(*N*-chloroacetylglucinato)-(1,10-phenanthroline-*N,N'*)-copper(II) dihydrate, as an example of a group I interaction with a large φ value ($r_{MM}=6.76$ Å and $\varphi=18.0^\circ$). The phen ligand interacts with the other ligand coordinated to the metal

and chelate- C_6 -ring overlaps (Fig. 8). Chelate-chelate overlaps do not occur, and metal ions are located outside of the phen ligand. In these structures, phen ligands interact with ions from the external sphere of the complexes, or a phen ligand from one complex interacts with the other ligand from the second complex. An example is the crystal structure of ((1*R*,2*R*)-1,2-diamino cyclohexane-*N,N'*)-(1,10-phenanthroline-*N,N'*)-platinum(II) bis(hexafluorophosphate) (refcode BEBCAN [44]) (Fig. 8). In this structure, the phen ligand interacts with the hexafluorophosphate ion from the external sphere of the complex, which is located above the other ligands in the vicinity of the metal ion.

In the NOBYOS crystal structure (Fig. 9) [45], which represents bis(*N*-chloroacetylglycinato)-(1,10-phenanthroline-*N,N'*)-copper(II) dihydrate, the r_{MM} value is 6.76 Å, similar to that of BEBCAN (Fig. 8), but ϕ is larger; 18.0°. Unlike in BEBCAN, the other two ligands are voluminous in NOBYOS. In this structure, there is a C–H...O interaction between the C–H group of the phen ligand and O atoms of the *N*-chloroacetylglycinato ligand.

Large r_{MM} values occur in the structures where an ion or molecule from the external sphere of the complex packs above the metal ion. In these structures, only pyridine and C_6 -rings participate in overlaps. The structure ZUH CAG [46], i.e., bis(μ_2 -phosphinato)-bis((1,10-phenanthroline)-

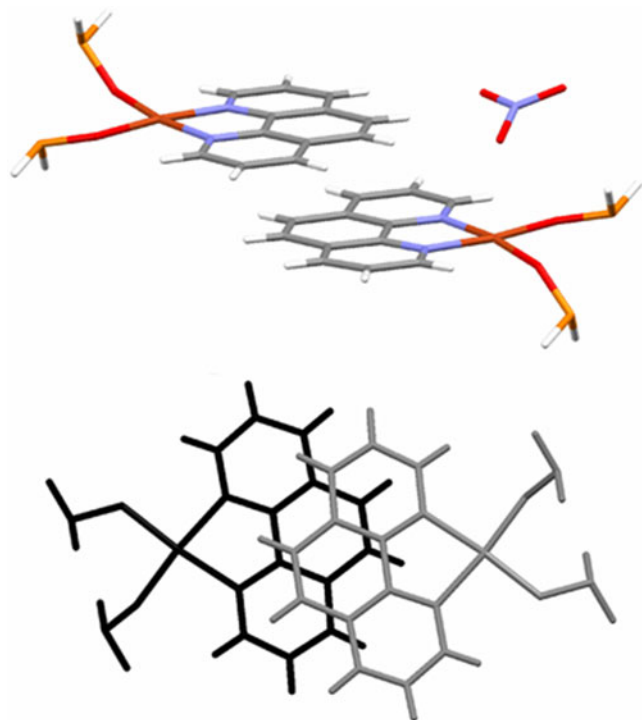


Fig. 10 Two projections presenting stacking interactions in the ZUH CAG crystal structure [46], i.e., bis(μ_2 -phosphinato)-bis((1,10-phenanthroline)-copper(II)) dinitrate, as an example of a group I interaction with a large value of r_{MM} and without mutually overlapping pyridine rings (r_{MM} =8.29 Å and ϕ =11.0°). The phen ligand interacts with the nitrite ion

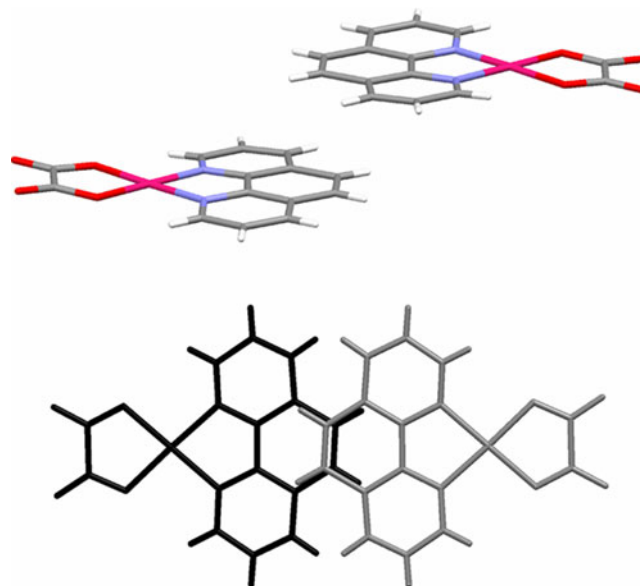


Fig. 11 Two projections presenting stacking interactions in the BIPGIR crystal structure [47], i.e., (oxalato-*O,O'*)-(1,10-phenanthroline-*N,N'*)-palladium(II) monohydrate, as an example of a group I interaction with only partially overlapping C_6 rings (r_{MM} =9.16 Å and ϕ =7.41°)

copper(II) dinitrate (Fig. 10), is an illustration of this overlap. In this structure, the phen ligand interacts with the nitrite ion, which is pseudo-coordinated to the Cu^{2+} ion. This structure is an example of an interaction that does not involve mutual overlap of the pyridine rings.

Large r_{MM} values and small ϕ values occur in the structures where only the C_6 rings (partially) overlap. An example of this—the (oxalato-*O,O'*)-(1,10-phenanthroline-*N,N'*)-palladium(II) monohydrate structure (refcode BIPGIR [47])—is shown in Fig. 11. In this structure, there is an additional stacking interaction with a third complex (Fig. 11).

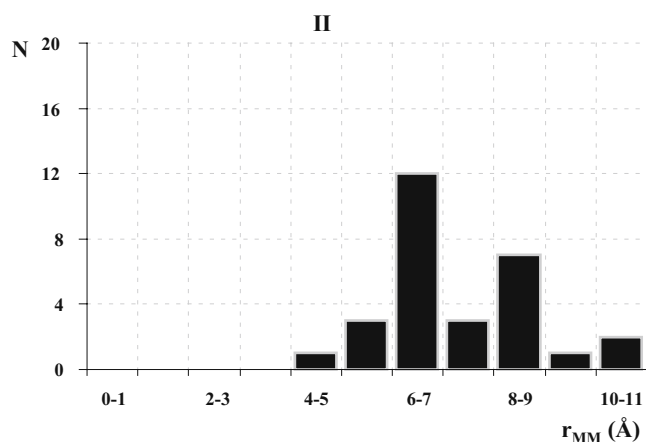


Fig. 12 Histogram of the distribution of r_{MM} values for group II interactions

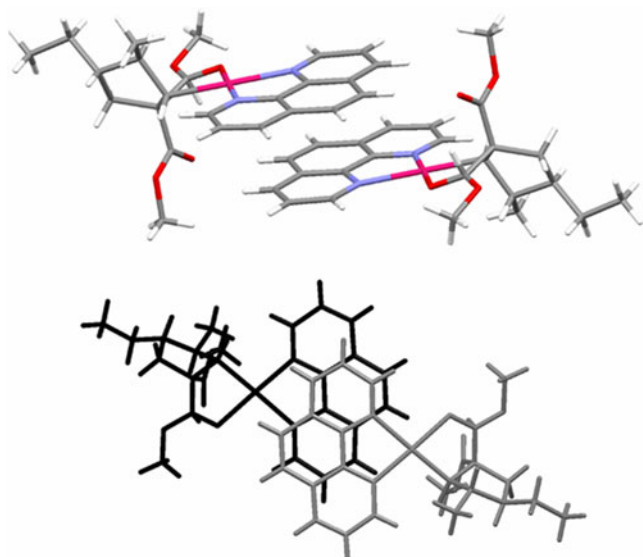


Fig. 13 Two projections presenting stacking interactions in the CAJNWX crystal structure [48], i.e., *trans,trans*-(1,10-phenanthroline)-(dimethyl-4-ethyl-5-methylcyclopentyl-2,2-dicarboxylate)-palladium(II) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, as an example of a group II interaction where pyridine, chelate and C₆-rings are involved in the overlap ($r_{MM}=6.12$ Å and $\varphi=20.2^\circ$)

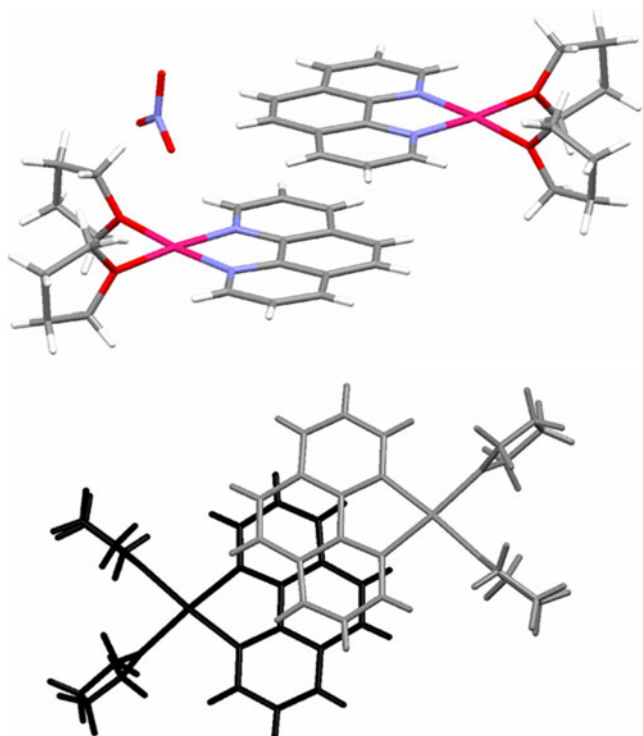


Fig. 14 Two projections presenting stacking interactions in the ILAHAE crystal structure [49], i.e., *cis*-(1,10-phenanthroline)-bis(tetrahydrofuran)-palladium(II) dinitrate, as an example of a group II interaction where chelate rings are not involved in the overlap ($r_{MM}=8.15$ Å and $\varphi=18.0^\circ$)

Structures that show group II interactions, which have a torsion angle T_1 that is close to 0° and a torsion angle T_2 that is close to 180° , comprise a smaller group (19 structures with 29 interactions) than group I structures. For this group, angle φ is larger than 20° , and values of r_{MM} are in the range 4.0–11.0 Å (mean value is 7.33 Å). In this group, phen ligands only partially overlap, and these partial overlaps always include at least one pyridine ring. In some structures, chelates and C₆-rings also participate in the overlap. The distribution of r_{MM} for group II is shown in Fig. 12.

The maximum of the distribution occurs in the range 6.0–7.0 Å, which corresponds to interactions in which chelate rings mainly participate in the overlap. In these structures, the other ligands are usually voluminous, and the stacking interaction is additionally stabilized by an interaction of a hydrogen atom on the phen ligand of one complex with the other ligand in the second complex. This type of stabilization is very commonly observed in the interactions of group II. An example of such an overlap is seen in the CAJNWX crystal structure [48], i.e., *trans,trans*-(1,10-phenanthroline)-(dimethyl-4-ethyl-5-methylcyclopentyl-2,2-dicarboxylate)-palladium(II) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (Fig. 13). In this structure, the phen ligand

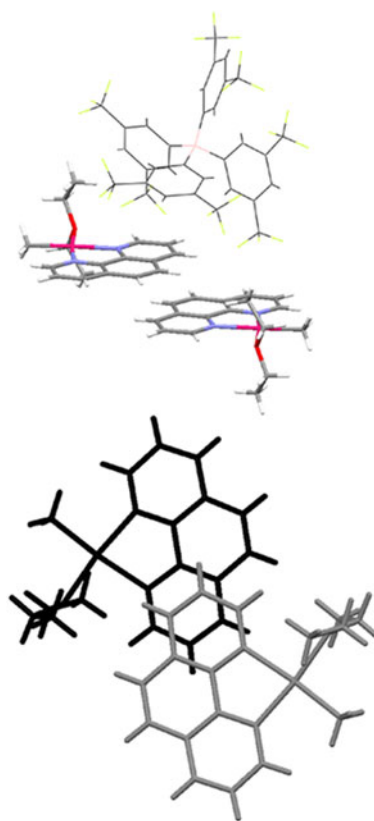


Fig. 15 Two projections presenting stacking interactions in the ZUKCAJ crystal structure [50], i.e., diethyloxymethyl-(1,10-phenanthroline-*N,N'*)-palladium(II) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, as an example of a group II interaction where only pyridine fragments are involved in the overlap ($r_{MM}=8.83$ Å and $\varphi=36.7^\circ$)

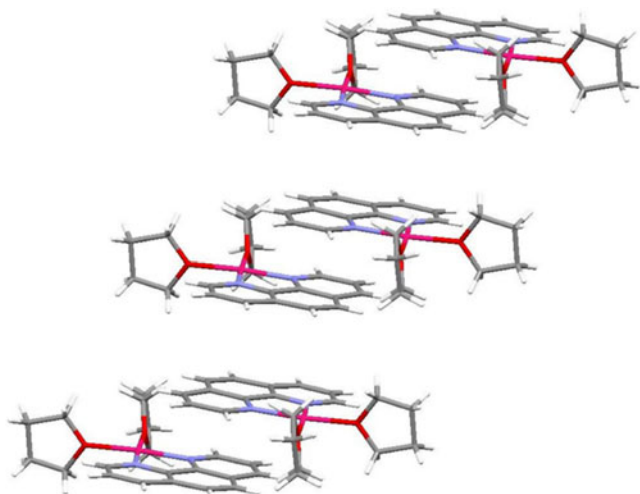


Fig. 16 The ILAHAE crystal structure [49], i.e., *cis*-(1,10-phenanthroline)-bis(tetrahydrofuran)-palladium(II) dinitrate, as an example of stacking chains with alternating overlaps; in this case, the overlaps are of types I and II

interacts with the other ligands, leading to a C–H...O interaction with a short H...O distance (2.394 Å).

In group II, the values of T_2 are close to 180° . This is connected with the large values of φ (Fig. 5), and there is a clear preference for pyridine–C₆-ring overlap. Pyridine–C₆-ring overlap gives a larger surface overlap than pyridine–pyridine, pyridine–chelate, or benzene–chelate overlap. This is particularly evident in structures in which chelate rings do not participate in the overlap. The packing in these structures is a consequence of the interaction of the phen complex with an ion or molecule from the external sphere that is pseudo-coordinated to the metal ion, or with other large ligands. The ILAHAE crystal structure [49], i.e., *cis*-(1,10-phenanthroline)-bis(tetrahydrofuran)-palladium(II) dinitrate (Fig. 14), is an illustration of this overlap. In this structure, the phen ligand interacts with nitrite ion that is pseudo-coordinated to the Pd²⁺ ion.

In the interactions with r_{MM} values above 7.0 Å and φ values above 30° , only one pyridine fragment of the

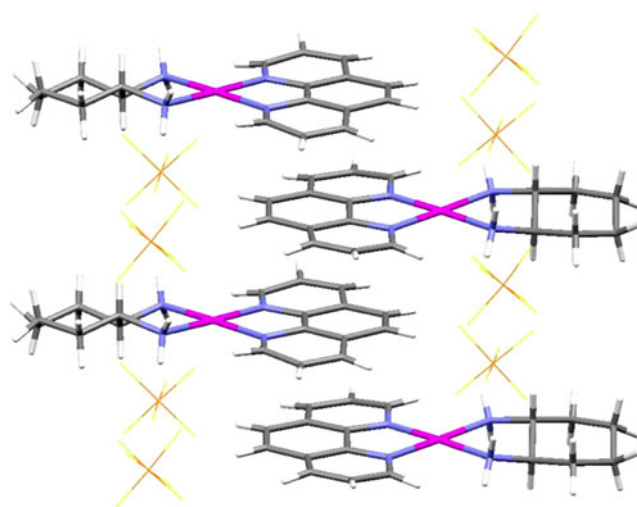


Fig. 17 The BEBCAN crystal structure [44], i.e., (1*R*,2*R*)-1,2-diaminocyclohexane-*N,N'*-(1,10-phenanthroline-*N,N'*)-platinum(II) bis(hexafluorophosphate), as an example of stacking chains in which the same overlap is repeated; in this case, an overlap of type I

complex is involved in the overlap. This type of overlap is very often a consequence of steric hindrance caused by the presence of another species that interacts with the π -system of the phenanthroline ligand, or by the presence of voluminous ligands.

An example is the structure of diethyloxymethyl-(1,10-phenanthroline-*N,N'*)-palladium(II) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (the ZUKCAJ crystal structure [50]), as shown in Fig. 15. In this structure, the tetrakis(3,5-bis(trifluoromethyl)phenyl)borate ion interacts with phenanthroline ligands, thus partially hindering the overlap of the phenanthroline ligands.

Packing in crystal structures

An analysis of packing in crystal structures of square-planar phen complexes showed that stacking interactions form

Table 1 Types of packing for different types of phen ligand overlap in square-planar complexes

Packing in the crystal structure	I		II		X	
	N_s	N_i	N_s	N_i	N_s	N_i
Stacking dimers	18	30	11	12	8	10
Chains with alternating overlaps	24	59	8	17	16	32
Chains with the same, constant overlap	3	4	0	0	3	4

I: group I interactions

II: group II interactions

X: interactions that do not belong to group I or group II

N_s : number of structures

N_i : number of interactions

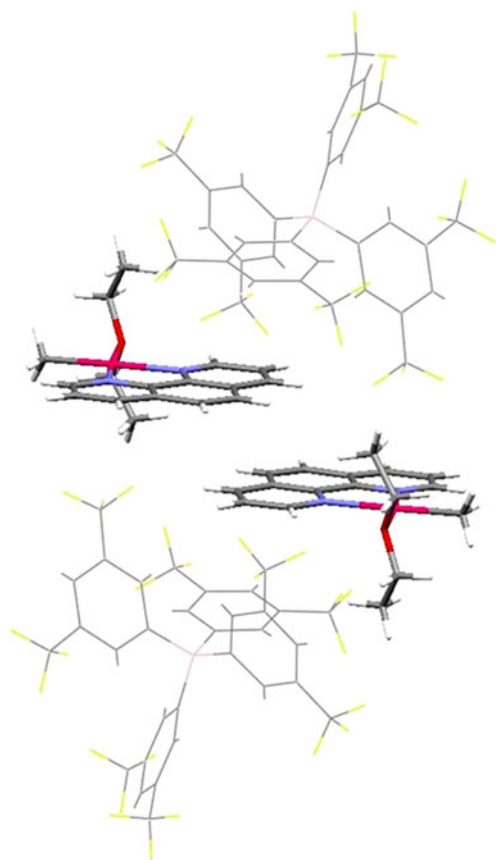


Fig. 18 The ZUKCAJ crystal structure [50], i.e., diethyloxymethyl-(1,10-phenanthroline-*N,N'*)-palladium(II) tetrakis(3,5-bis(trifluoromethyl)phenyl) borate, as an example of a crystal structure where the stacking interactions form dimers

stacking chains and dimers. We analyzed the packing in all structures, regardless of their torsion angles T_1 and T_2 (i.e., not only structures belonging to groups I and II, which have T_1 close to 180° and T_2 close to 0° or 180°). In the crystal structures of phen complexes, we found 116 stacking chains and 52 stacking dimers. In some chains, the same overlap was constantly repeated, while in others, two types of overlap appeared alternately in the chains.

Stacking chains

Chains with alternating overlaps were noted in 35 structures (108 interactions). An example of a structure with a chain with alternating overlaps is shown in Fig. 16. In these chains, the most frequent interactions are those of group I, with the torsion angle T_2 close to 0° . In 24 group I structures we found 59 interactions in chains with alternating overlaps. Group I interactions show a preference for alternating overlaps. However, the interactions seen in chains with alternating overlaps often do not belong to either group I or group II, and this is their preferred way of packing (Table 1).

Stacking chains that repeat the same overlap were noted in only a very small number of structures (5; 8 interactions, see Fig. 17). In these chains, torsion angle T_2 is often close to 0° (group I), or the overlaps do not belong to group I or group II. There is only one case where an interaction with T_2 close to 180° (group II) forms stacking chains with the same overlap.

Stacking dimers

Stacking dimers, like the packing seen in crystal structures of phen complexes, were seen in 29 structures (52 interactions). The most frequent interactions in these structures were those of group I (T_2 close to 0°), with 18 structures. However, other values of torsion angle T_2 were also very common in dimers; see Table 1. An example of a dimer is shown in Fig. 18.

Conclusions

Eighty-one structures with 172 stacking interactions of phen square-planar complexes were found in the Cambridge Structural Database (CSD). The distributions of the torsion angles T_1 and T_2 show that the two interacting complexes are oriented “head to tail” in most of the interactions, with a large portion of the phen ligand involved in the overlap.

In our previous work [36], we showed that it was possible to classify interactions between terpy complexes into six types based on the clustering in a scattergram of the angle φ versus the displacement r_{MM} . All interactions of the same type were clustered together on the scattergram and had very similar overlap patterns. However, the scattergram of φ versus r_{MM} for phen complexes did not show clustering. Also, the ranges of φ and r_{MM} were quite different for terpy and phen complexes, indicating different modes of the overlap for these complexes. Phen complexes show many different overlap geometries in stacking interactions, but short metal–metal distances were not observed. The geometry of the interaction is very often influenced by the two ligands coordinated at the third and fourth coordinating positions, or by ions in the crystal structure. Stacking interactions of phen square-planar complexes result in the formation of chains and dimers in crystal structures, and stacking chains with alternating overlaps are the predominant type of packing for these complexes.

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References

1. Sato T, Tsuneda T, Hirao K (2005) *J Chem Phys* 123:104307–104317
2. Grimme S (2008) *Angew Chem Int Ed* 47:3430–3434
3. Yurtsever E (2009) *J Phys Chem A* 113:924–930
4. Rubeš M, Bludsky O, Nachtigall P (2008) *Chem Phys Chem* 9:1702–1708
5. Lee EC, Kim D, Jurecka P, Tarakeshwar P, Hobza P, Kim KS (2007) *J Phys Chem A* 111:3446–3457
6. Sinnokrot MO, Sherrill CD (2006) *J Phys Chem A* 110:10656–10668
7. Podeszwa R, Bukowski R, Szalewicz K (2006) *J Phys Chem A* 110:10345–10354
8. Pitonak M, Neogrady P, Rezac J, Jurecka P, Urban M, Hobza P (2008) *J Chem Theor Comput* 4:1829–1834
9. Tewari AK, Dubey R (2008) *Bioorgan Med Chem* 16:126–143
10. Sponer J, Riley KE, Hobza P (2008) *Phys Chem Chem Phys* 10:2595–2610
11. Tomić ZD, Novaković SB, Zarić SD (2004) *Eur J Inorg Chem* 11:2215–2218
12. Sredojević DN, Tomić ZD, Zarić SD (2007) *Cent Eur J Chem* 5:20–31
13. Chowdhury S, Drew MGB, Datta D (2003) *Inorg Chem Commun* 1014–1016
14. Tomić ZD, Sredojević DN, Zarić SD (2006) *Cryst Growth Des* 6:29–31
15. Castineiras A, Sicilia-Zafra AG, Gonzales-Perez JM, Choquesillo-Lazarte D, Niclos-Gutierrez J (2002) *Inorg Chem* 41:6956–6958
16. Craven E, Zhang C, Janiak C, Rheinwald G, Lang H (2003) *Z Anorg Allg Chem* 629:2282–2290
17. Mukhopadhyay U, Choquesillo-Lazarte D, Niclos-Gutierrez J, Bernal I (2004) *Cryst Eng Comm* 6:627–632
18. Pucci D, Albertini V, Bloise R, Bellusci A, Cataldi A, Catapano CV, Ghedini M, Crispini A (2006) *J Inorg Biochem* 100:1575–1578
19. Mosae SP, Suresh E, Subramanian PS (2009) *Polyhedron* 28:245–252
20. Wang XJ, Jian HX, Liu ZP, Ni QL, Gui LC, Tang LH (2008) *Polyhedron* 27:2634–2642
21. Sredojević DN, Bogdanović GA, Tomić ZD, Zarić SD (2007) *Cryst Eng Comm* 9:793–798
22. Mitchell JBO, Nandi CL, McDonald IK, Thornton JM, Price SL (1994) *J Mol Biol* 239:315–331
23. Wang X, Sarycheva OV, Koivisto BD, McKie AH, Hof F (2008) *Org Lett* 10:297–300
24. Ostojić BD, Janjić GV, Zarić SD (2008) *Chem Commun* 6546–6548
25. Bogdanović GA, Medaković VB, Milčić MK, Zarić SD (2004) *Int J Mol Sci* 5:174–185
26. Medaković VB, Milčić MK, Bogdanović GA, Zarić SD (2004) *J Inorg Biochem* 98:1867–1873
27. Boyd PDW, Hosseini A (2006) *Acta Crystallogr E* 62:2081–2083
28. Jiang YF, Xi CJ, Liu YZ, Niclos-Gutierrez J, Choquesillo-Lazarte D (2005) *Eur J Inorg Chem* 8:1585–1588
29. Philip V, Suni V, Kurup MRP, Nethaji M (2004) *Polyhedron* 23:1225–1233
30. Tsubaki H, Tohyama S, Koike K, Saitoh H, Ishitani O (2005) *Dalton Trans* 2:385–395
31. Abram U, Castineiras A, Garcia-Santos I, Rodriguez-Riobo R (2006) *Eur J Inorg Chem* 15:3079–3087
32. Granifo J, Vargas M, Garland MT, Ibanez A, Gavino R, Baggio R (2008) *Inorg Chem Commun* 1388–1391
33. Stojanović SD, Medaković VB, Predović G, Beljanski M, Zarić SD (2007) *J Biol Inorg Chem* 12:1063–1071
34. Sredojević DN, Tomić ZD, Zarić SD (2010) *Cryst Growth Des* 10:3901–3908
35. Janiak C (2000) *J Chem Soc Dalton Trans* 3885–3896
36. Janjić GV, Andrić J, Kapor A, Bugarčić ŽD, Zarić SD (2010) *Cryst Eng Comm* 12:3773–3779
37. Constable EC, Chaurin V, Housecroft CE, Neuburger M, Schaffner S (2008) *Cryst Eng Comm* 10:1063–1069
38. Bodoki A, Hangan A, Oprean L, Alzuet G, Castiñeiras A, Borrás J (2009) *Polyhedron* 28:2537–2544
39. Schaeffer F, Rimsky S, Spassky A (1996) *J Mol Biol* 260:523–539
40. Allen FH (2002) *Acta Crystallogr B* 58:380–388
41. Allen FH, Davies JE, Galloy JJ, Johnson O, Kennard O, Macrae CF, Mitchell EM, Mitchell GF, Smith JM, Watson DG (1991) *J Chem Inf Comput Sci* 31:187–204
42. Allen FH, Kennard O, Watson DG, Brammer L, Guy Orpen A, Taylor R (1987) *J Chem Soc Perkin Trans II*:S1–S19
43. Wang Y, Okabe N (2005) *Chem Pharm Bull* 53:366–373
44. Koshiyama T, Kato M (2003) *Acta Crystallogr C* 59:446–449
45. Menabue L, Saladini M, Bavoso A, Ostuni A (1998) *Inorg Chim Acta* 268:205–210
46. Parker JO, Harvey RM, Breneman GL (1996) *Acta Crystallogr C* 52:871–873
47. Odoko M, Wang Y, Okabe N (2004) *Acta Crystallogr Sect E* 60:1825–1827
48. Goj LA, Widenhoefer RA (2001) *J Am Chem Soc* 123:11133–11147
49. Huang H, Yu SY (2003) *Chin J Struct Chem (Jiegou Huaxue)* 22:547–549
50. Rix FC, Brookhart M, White PS (1996) *J Am Chem Soc* 118:2436–2448