DALTON
FULL PAPER

A critical account on π–π stacking in metal complexes with aromatic nitrogen-containing ligands †

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Received 14th April 2000, Accepted 21st June 2000
First published as an Advance Article on the web 22nd September 2000

A geometrical analysis has been performed on π–π stacking in metal complexes with aromatic nitrogen-containing ligands based on a Cambridge Structural Database search and on X-ray data of examples in the recent literature. It is evident that a face-to-face π–π alignment where most of the ring-plane area overlaps is a rare phenomenon. The usual π interaction is an offset or slipped stacking, *i.e.* the rings are parallel displaced. The ring normal and the vector between the ring centroids form an angle of about 20° up to centroid–centroid distances of 3.8 Å. Such a parallel-displaced structure also has a contribution from π–σ attraction, the more so with increasing offset. Only a limited number of structures with a near to perfect facial alignment exists. The term π–π stacking is occasionally used even when there is no substantial overlap of the π-ring planes. There is a number of metal–ligand complexes where only the edges of the rings interact in what would be better described a C–H · · · π attraction.

Introduction

Aromatic–aromatic or π–π interactions are important non-covalent intermolecular forces similar to hydrogen bonding. They can contribute to self-assembly or molecular recognition processes when extended structures are formed from building blocks with aromatic moieties.[1,2] As such, π–π interactions range from large biological systems to relatively small molecules.[3–7] Non-covalent interactions between aromatic groups play a role in the binding and conformations all the way from nucleic acids and proteins[8–12] to benzene.[13] Calculations give an energy of about 2 kJ mol^{-1} for a typical aromatic–aromatic π-stacking interaction.[14]

In the area of metal–ligand compounds, the importance of information gained from crystal structures on the covalent metal–ligand bond distances and angles has often overshadowed the additional information available from them: how the complexes or co-ordination polymers are packed in the crystal lattice. While hydrogen bonding is now usually pointed out as a packing motif, the possibility of π–π interactions is mostly not well documented in the structure discussion. However, the understanding and utilization of all non-covalent interactions including π–π stacking is of fundamental importance for the further development of (inorganic) supramolecular chemistry and the tuning and prediction of crystal structures.[2,15,16,] Recently an increased reference of π–π interactions can be noted. Yet, still few details are given. Also, the term "π–π interaction" appears often to be used indiscriminately. One sometimes gets the impression that scientists expect that aromatic rings will self-interact through π–π parallel stacking interaction. This expectation is erroneous, however. Simple aromatic residues prefer to associate *via* enthalpically favorable edge-to-face C–H · · · π interactions.[11,17] With this article the awareness for the importance and description of stacking interactions should be raised among the inorganic community. Described here are the so-called π–π interactions of metal complexes with aromatic nitrogen-containing ligands. The intention is to assess the relative orientation, *i.e.* the overlap of the ring planes. Nitrogen-containing ligands were chosen as the focus because they feature prominently in the construction of co-ordination polymers and supramolecular co-ordination chemistry.[18,19]

The different types and the nature of aromatic–aromatic interactions

In the arrangement of aromatic rings one can distinguish generally between a stacked arrangement and an edge- or point-to-face, T-shaped conformation (Fig. 1). The T-shaped conformation is a C–H · · · π interaction.[20–22] Stacking does not necessarily have to be a perfect face-to-face alignment of the atoms but can also be an offset or slipped packing. Both face-to-face and T-shaped conformations are limiting forms in aromatic interactions. Among these, the stacked (facial) arrangements are of particular interest as π–π interactions. A sizeable number of theoretical and experimental studies have been performed to understand the nature of π–π interactions. While there is considerable experimental evidence on the structure and property influencing character of these interactions, their true nature is still a matter of some discussion.[3,5–7,12]

The following electrostatic or van-der-Waals interactions are discussed as intermolecular forces[23] for the stabilization of π–π interactions between closed-shell molecules;[5,24] (Fig. 2 gives a pictorial summary of the interactions). (a) Dipole–dipole (electrostatic) interactions: the interactions between the different permanent and static molecular charge distributions. (b) Dipole–induced-dipole interactions between the static molecular charge distribution of group A with a proximity-induced change in charge distribution of group B. (c) Induced-dipole–induced-dipole (London) dispersion interaction: the instantaneous dipole moment from a fluctuating electron cloud polarizes a neighboring molecule and induces in it also an instantaneous dipole. These van-der-Waals interactions (a)–(c) are inherently attractive and their potentials fall off rapidly with distance by $1/r^6$. (d) Pauli repulsion: at very short distances the filled electron clouds of the interacting molecules begin to overlap and the (Pauli) repulsion between the electron shells

† Based on the presentation given at Dalton Discussion No. 3, 9–11th September 2000, University of Bologna, Italy.

Dedicated to Professor Dr. Herbert Schumann on the occasion of his 65th birthday.

DOI: 10.1039/b003010o

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becomes dominating. (e) Solvophobic effects: in polar solvents, solvophobic effects leading to desolvation can stabilize an aggregation of lipophilic molecular surfaces, *e.g.* π systems.[6] (f) Charge transfer: charge transfer or electron donor–acceptor effects refer to a stabilization due to mixing of a ground state $A \cdots B$ with an excited charge-separated state $A^+ \cdots B^-$. Such coulomb attractions based on charge transfer are generally viewed as negligible.[5,6,25,26] (Such charge transfer effects are different from static π-electron donor–acceptor complexes; see below.)

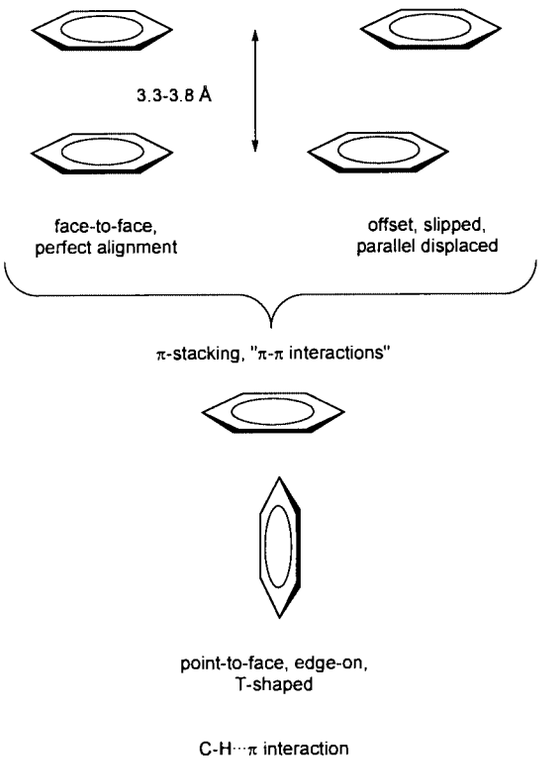


Fig. 1 Principal orientations of aromatic–aromatic interactions.

From the yet incomplete understanding of facial aromatic interactions it is clear that the term "π–π interactions" is not very well defined. It is commonly used for stacks of aromatic groups with approximately parallel molecular planes separated by interplanar distances of about 3.3–3.8 Å. Hence, within this article the term "π–π interaction" is used for non-covalent interactions between π systems without implying anything on the origin of this interaction.

Benzene immediately comes to mind as a prototypical model for aromatic interactions, especially since early stack formations were discovered in polyaromatic hydrocarbons such as pyrene and coronene.[27,28] Benzene is definitely the ideal π system and as such was also studied theoretically concerning aromatic–aromatic packing interactions.[4,5,13,29] For a benzene dimer the T-shaped motif is found to be more stable than the face-to-face stacked one. Fig. 2(d) illustrates the electrostatic (Pauli) repulsion between the negatively charged (out-of-plane) π electrons in the face-to-face stacked orientation. In Fig. 3 the attractive interaction between the positively charged hydrogen atoms (or σ framework) and the π electrons is shown. The point- or edge-to-face, edge-on or T-shaped arrangement can be seen as the origin of the well known herringbone structure of crystalline benzene.[29,30] It is also the motif of arene interaction in many protein structures with an interaction energy of 4 to 8 kJ mol^{-1}.[8,10,11,17] Also, in a substantially offset π-stacked geometry, included in Fig. 3, π–σ attraction can dominate. Such a parallel-displaced dimeric structure may be even lower in energy than the T-shaped benzene dimer.[31] Thus, studies on benzene arrive at the conclusion that there is no basis for an

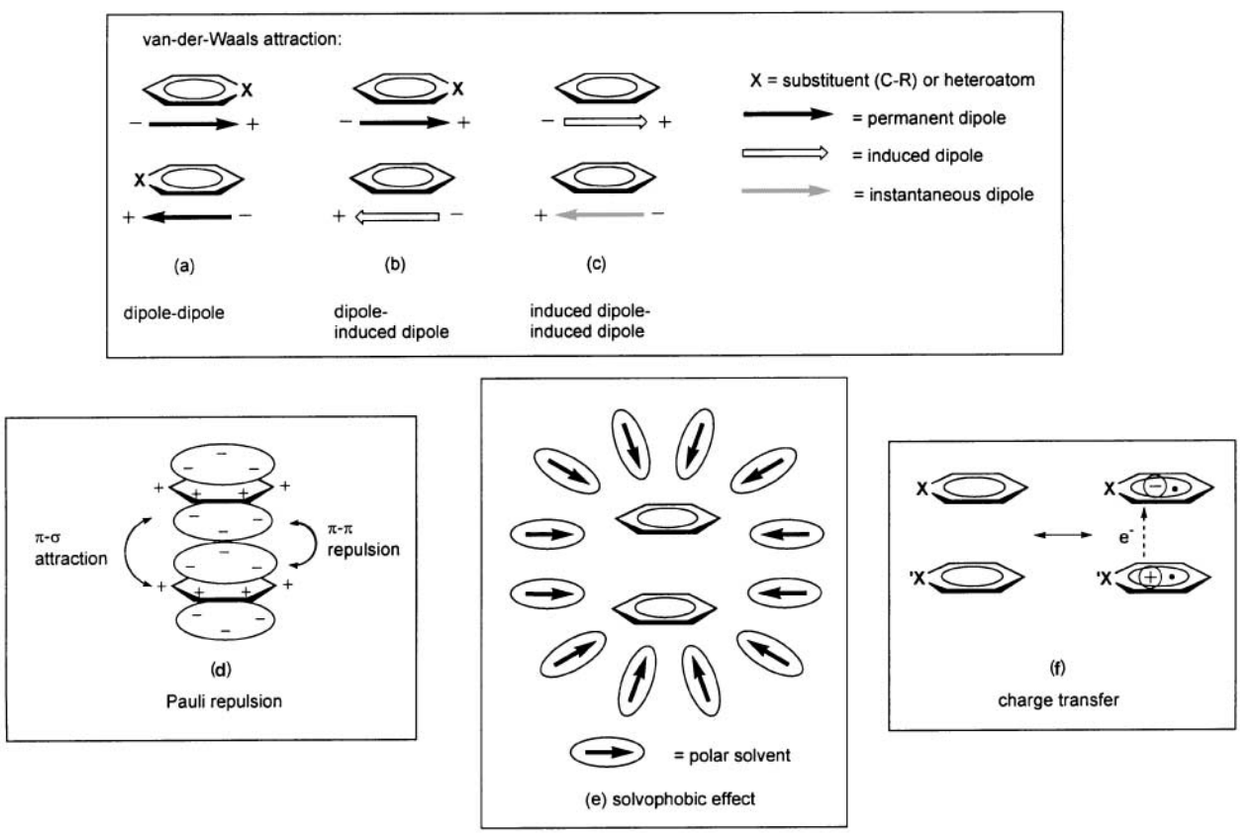


Fig. 2 Schematic illustration of the electrostatic interactions between two arene moieties. For simplicity the two arene moieties are drawn in perfect face-to-face alignment.

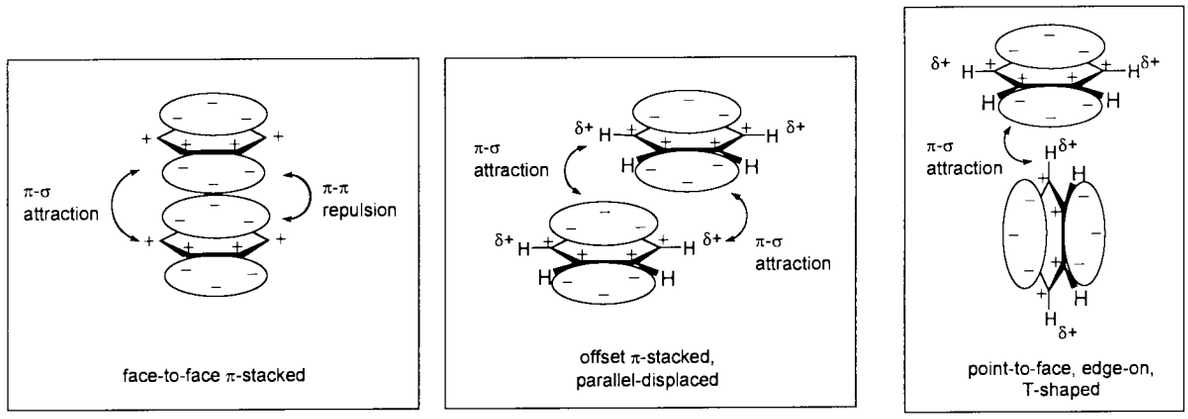


Fig. 3 Schematic illustration of the attractive electrostatic interaction between the σ framework and the π electron density in an offset π-stacked and in a T-shaped geometry because of decreased π–π repulsion.

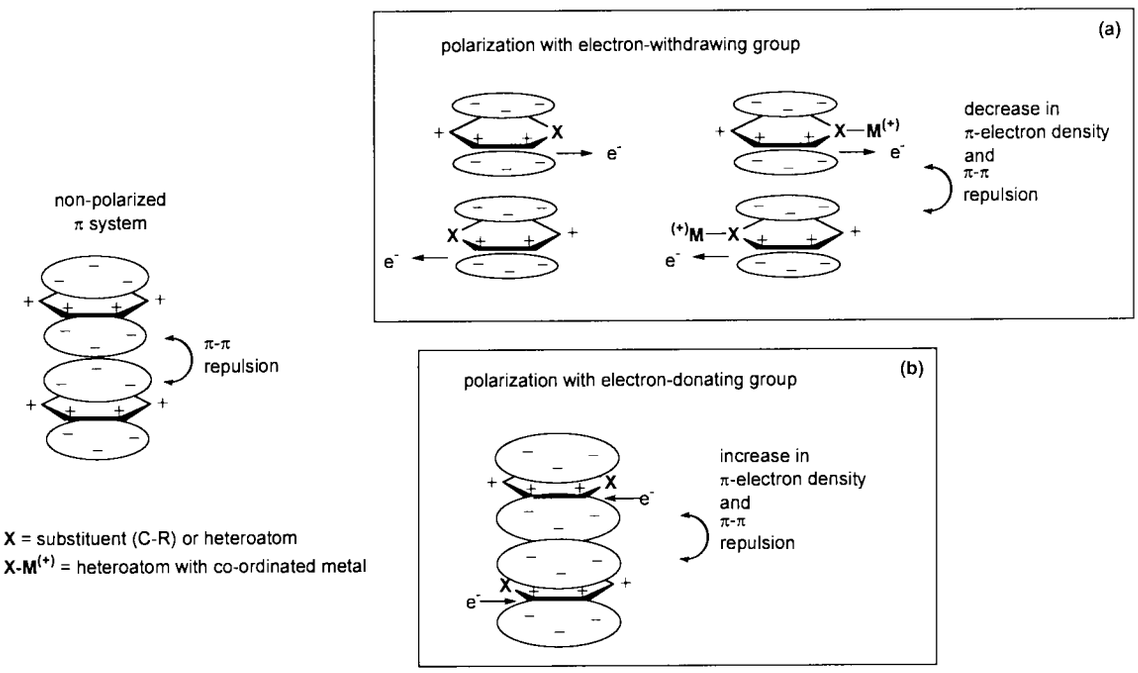


Fig. 4 Direction of substituent, heteroatom or heteroatom–metal effects with respect to π–π repulsion: (a) electron withdrawing groups decrease, (b) electron donating groups increase the π-electron density and, hence, their repulsion. For simplicity the arene moieties are drawn in perfect face-to-face alignment and with a uniform decrease or increase in π-electron density. Not shown is the still present π–σ attraction which competes with π–π repulsion.

aligned face-to-face stacking. In reality, one deals, however, with π systems which are extended or polarized through substituents or heteroatoms. Enlargement or polarization of the π system changes the picture and conclusions drawn for benzene quite drastically. For example, stacked structures become increasingly favorable with increasing arene size.[32] Larger systems such as pyrene or coronene show an offset π stacking with the hydrogens roughly over ring centers.[14,27,33] As such, non-polarized benzene is not necessarily a good model to arrive at an understanding of π–π interactions.

A full account of the intermolecular interactions (a) to (f) outlined above and in Fig. 2 would require high-level and time-consuming calculations which are inaccessible for the practical chemist. Qualitatively to understand and analyse aromatic–aromatic interactions, Hunter and Sanders have devised a set of rules based on a simple model of the charge distribution in a π system.[7] They separated the σ framework and the π electrons and assumed that π–π interactions are the result of π–σ attractions that overcome π–π repulsions (*cf.* Figs. 3 and 4). These "Hunter-Sanders" rules state for non-polarized π-systems: rule 1, π–π repulsion dominates in a face-to-face π-stacked geometry; rule 2, π–σ attraction dominates in an edge-on or T-shaped geometry; rule 3, π–σ attraction dominates in an offset π-stacked geometry. For polarized π systems there are an additional three rules which are stated here in the form of a requirement for face-to-face π-stacking: rule 4, for interaction between highly charged atoms, charge–charge interaction dominates; rule 5, a favorable (face-to-face) interaction with a neutral or weakly polarized site requires as a π polarization a π-deficient atom (in the aromatic ring); rule 6, a favorable (face-to-face) interaction with a neutral or weakly polarized site requires as a σ polarization a positively charged atom (in the aromatic ring).

These rules do not state that a π–π interaction will occur, since such intermolecular interactions have additional strong geometric requirements which may not be available. However, the rules indicate how (host–guest) systems with efficient π stacking should be designed. If π–π interactions are observed the Hunter–Sanders rules seem to allow for their qualitative understanding.[5–7] I note that the π–π theory by Hunter and Sanders has been criticized: the introduction of σ and π charges was seen as redundant and the role of molecular quadrupoles was emphasized.[13] It appears that this criticism was mainly based on theoretical investigations of non-polar arenes.

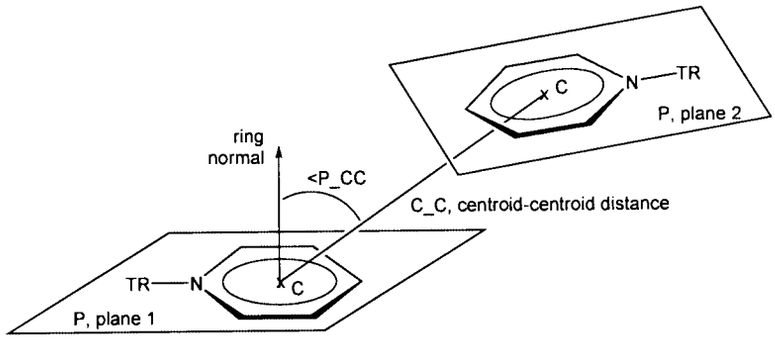
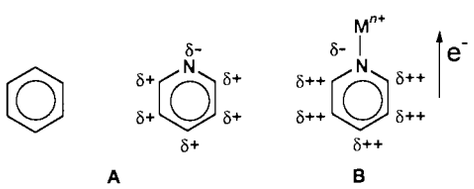


Fig. 5 Definition of two transition-metal pyridine fragments. TR = Transition metal, C = ring centroid, P = pyridine plane, P–CC = angle between the ring normal of the pyridine plane and the centroid vector. The centroid–centroid distance (C–C) was constrained to an *inter*molecular (group) contact between 3.0 and 4.6 Å for the search. Out of 207507 entries in the database 4818 structures with this constraint were found which gave 7620 data sets (multiple contacts for some structures). Angles were transformed to values between 0 and 90° through application of the sin and arcsin function.

Substituents or heteroatoms perturb the uniform charge distribution in benzene. Partial atomic charges and a permanent dipole result which introduce electrostatic dipole–dipole and dipole–induced dipole interactions as shown in Fig. 2(a), (b). In addition, they strongly affect atom–atom and atom–(out-of-plane) π-electron interactions which were illustrated in Fig. 2(d).[5,7] Experimental investigations showed that electron withdrawing substituents or heteroatoms lead to the strongest π–π interaction. They decrease the π-electron density in the rings and subsequently the important π-electron repulsion which was indicated in Fig. 2(d). The face-to-face π stacking of aromatic moieties shows increased stability when *both* partners are electron-poor, whereas electron donating substituents disfavored a π–π interaction. The π-electron density within the rings is increased and so is the π-electron repulsion.[6,25,34]

The order of stability in the interaction of two π systems is π-deficient–π-deficient > π-deficient–π-rich > π-rich–π-rich.[7,34] Fig. 4 outlines the direction of substituent or heteroatom effects with respect to an electrostatic repulsion of the π-electron densities. π–π Stacking interactions between π-donor and π-accepting ring systems have, however, elegantly been exploited in the self-assembly work of Stoddart and co-workers[1] and Foster.[35]

Electron donors are, for example, R, OR, NH_2 and NR_2 (R = alkyl). Electron acceptors are, for example, F, NO_2, CO_2Me and =O (in *para*-benzoquinone).[7,25,34] A nitrogen heteroatom within the ring is also an electron-withdrawing perturbation. Pyridine, bipyridines and other aromatic nitrogen heterocycles are known as electron poor ring systems (**A**) (relatively inert to electrophilic attack, enhanced reaction with nucleophiles).[36] A metal which is co-ordinated to a nitrogen heteroatom will further enhance the electron-withdrawing effect through its positive charge (**B**). Hence, aromatic nitrogen heterocycles should in principle be well suited for π–π interactions because of their low π-electron density. The introduction of heterocyclic N increases the tendency to stack.



π–π Stacking between nitrogen-containing aromatic ligands

Multidentate ligands with pyridine groups or nitrogen heterocycles in general feature prominently as building blocks in the design of metal–ligand networks.[15,18] π–π Stacking is an increasingly noted feature in the structural description of metal complexes with these ligands. Furthermore, it is not just a structural phenomenon but also correlated with the solid-state luminescence properties of some metal complexes, notably with platinum[37,38] but also with gold[39] and other metals.[40] At the same time, few details on the π interaction aside from the interplane distance are usually given. A closer look at the so-called π–π interactions reveals that the term appears to be used for all degrees of slipped stacking. It could even involve a marked degree of deviation from coplanarity, *i.e.* an angular orientation of the ring planes towards a C–H···π interaction.[20]

A CSD search

A Cambridge Structural Database (CSD) search has been performed using the QUEST3D routine. The results are depicted by the program CSD VISTA. The search was based on the definition of two transition-metal pyridine fragments (Fig. 5) or two transition-metal quinoline fragments (Fig. 6). The pyridine or quinoline ring could be part of larger extended ring systems.

The results of the pyridine-fragment search are as follows: centroid–centroid contacts between two pyridine fragments start slightly below 3.4 Å and a relative maximum in the number of examples is found around 3.8 Å (Fig. 7). The vast majority of intermolecular plane contacts is close to parallel to each other, *i.e.* the interplane angle is near zero (Fig. 8). Yet, the two pyridine rings are parallel displaced with respect to each other. The displacement was measured by the angle formed between the ring-centroid vector (CC) and the ring normal to one of the pyridine planes. This angle averages 27° for the 7620 data sets. Most examples lie between displacement angles of 16 and 40° (Fig. 9). A correlation between the displacement angle and the centroid–centroid distance (Fig. 10) reveals a slightly smaller tendency for parallel displacement at shorter distance. For ring centroid contacts below 3.8 Å the displacement angle is around 20°.

At a centroid contact of 3.80 Å an angle of 20° between the ring normal and the centroid vector corresponds to a horizontal displacement of 1.30 Å, *i.e.* a shift of almost one C–C bond length from the face-to-face alignment (**C**). This translates to a π–π stacking interaction which is quite often observed: the ring planes are offset such that a ring atom lies almost over the center of the other ring and its hydrogen atom almost on top of a carbon atom (see below).

Examples of structures with a zero or near zero displacement angle and (almost) parallel ring planes, *i.e.* a near to perfect face-to-face alignment, are (C–C contact given in parentheses):

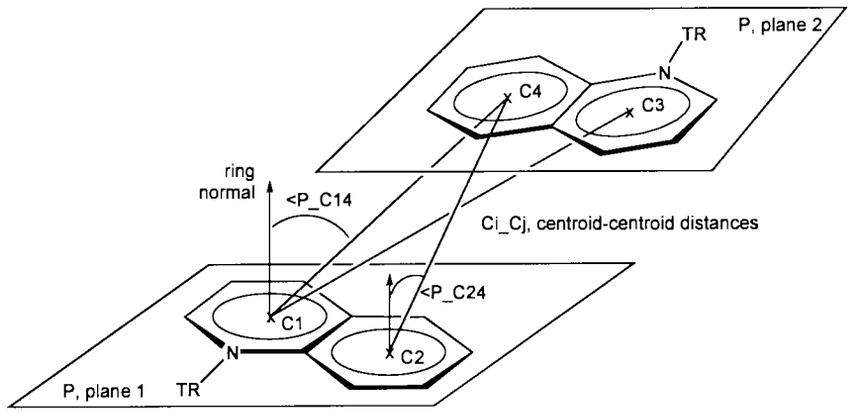


Fig. 6 Definition of two transition metal quinoline fragments. TR = Transition metal, C*i*,*j* = ring centroids, P = quinoline plane, P–C*ij* = angle between the ring normal of the quinoline plane and the centroid vector C*i*–C*j*. The overall distance between the two quinoline centers was constrained to an *inter*molecular (group) contact between 3.0 and 5.0 Å for the search. Out of 207507 entries in the database 718 structures with this constraint were found which gave 980 data sets (multiple contacts for some structures). Angles were transformed to values between 0 and 90° through application of the sin and arcsin function.

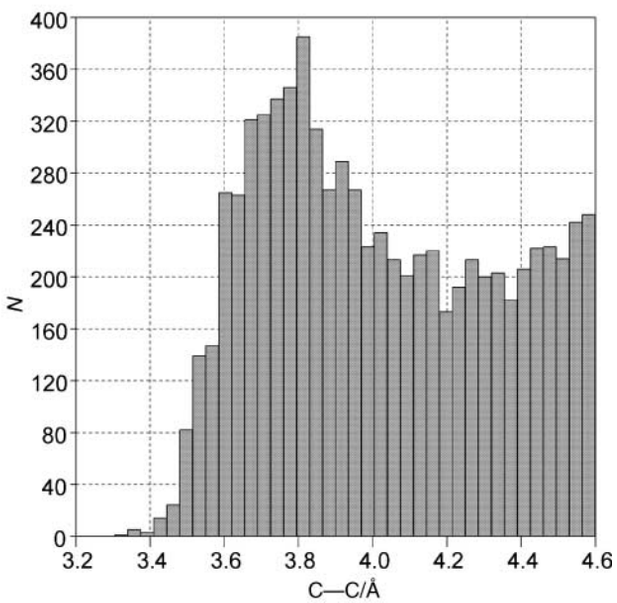
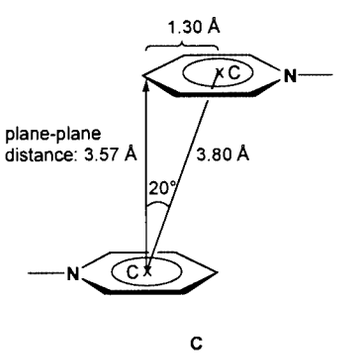


Fig. 7 Histogram for the centroid–centroid distance between two pyridine–metal fragments from a CSD search as outlined in Fig. 5. The centroid–centroid distance (C–C) was constrained to an *inter*-molecular (group) contact between 3.0 and 4.6 Å for the search.



c

(2,2′-bipyridyl-*N*,*N*′)–dicyanoplatinum(II) and –palladium(II) (3.33 and 3.354 Å),[41] bis(*N*-benzoylphenylalanine)phenanthrolinecopper(II) monohydrate (3.467 Å),[42] pyridine(salicylaldehyde *S*-methylthiosemicarbazonato)copper(II) nitrate (3.497 Å),[43] bis((2,9-dimethyl-1,10-phenanthroline)(*o*-toluenethiolato-*S*)copper(I)) (3.551 Å),[44] and dichlorobis(pyridine)-cobalt(II) (3.660 Å).[45]

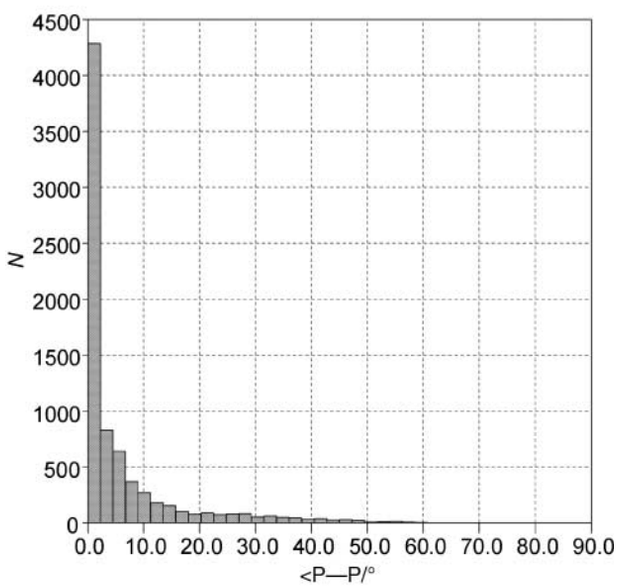


Fig. 8 Histogram for the plane–plane angle between two pyridine-metal fragments from a CSD search as outlined in Fig. 5.

To test for possible changes in the approach of nitrogen heterocycles with extended π systems, a separate CSD search was carried out on the interaction between two transition-metal quinoline fragments as depicted in Fig. 6. Such a π–π interaction may only involve part of the ring system. Hence, one can differentiate the approach of the two pyridine moieties, the two arene rings and the approach of the arene to the pyridine ring. The histograms in Fig. 11 indicate that all three contacts can be found. From the number of hits up to centroid–centroid distances of 3.8 Å there is a preference for the pyridine–arene approach, followed by the arene–arene approach. Pyridine–pyridine type interactions are much less important. Again, the majority of intermolecular plane contacts is close to parallel to each other (Fig. 12). Also, the ring sections are parallel displaced with respect to each other. Fig. 13 shows the distribution in displacement angle for the pyridine–arene ring contact as an example. Scattergrams for the correlation between the displacement angle and the centroid–centroid distance (Fig. 14) reveal again a slightly smaller tendency for parallel displacement at shorter distance. For centroid–centroid distances up to 3.8 Å the displacement angle lies around 20°. This value is quite similar to what can be observed for the basic pyridine–pyridine approach in Fig. 10.

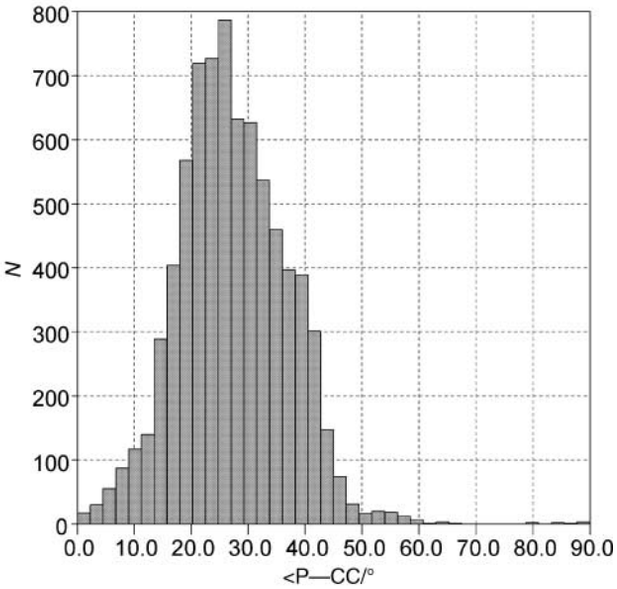


Fig. 9 Histogram for the displacement angle P–CC defined as the angle between the ring-centroid vector (CC) and the ring normal to one of the pyridine planes. For further details of the CSD search see caption to Fig. 5.

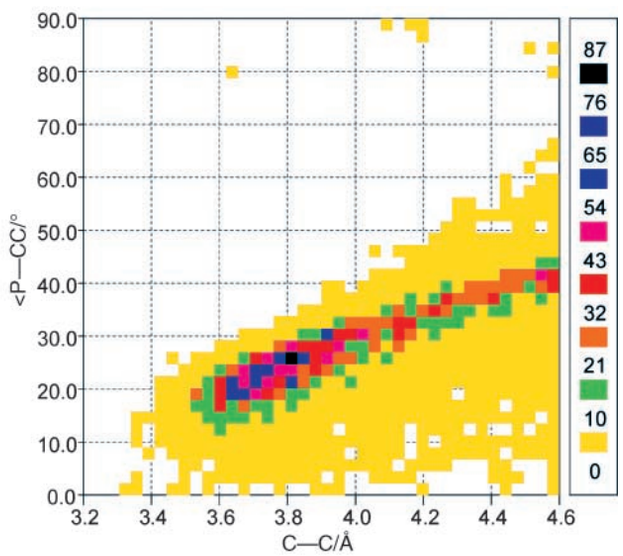


Fig. 10 Scattergram for a correlation between the displacement angle (P–CC) and the centroid–centroid distance (C–C). For further details of the CSD search see also Fig. 5.

Structures with a zero or near zero displacement angle and (almost) parallel ring planes, *i.e.* a near to perfect face-to-face alignment, can be found in particular for the stacking interaction of the arene–arene moieties. Examples are (C2–C4 distance given in parentheses): Dichlorobis(1,10-phenanthroline)-iron(III) tetrachloro(1,10-phenanthroline)ferrate(III) acetonitrile solvate (3.420 Å),[46] carbonatobis(1,10-phenanthroline)-cobalt(III) bromide tetrahydrate (3.455 Å),[47] *fac*-μ-cyano-bis-[tricarbonyl(1,10-phenanthroline)manganese] hexafluorophosphate (3.460 Å),[48] tricarbonyl(1,10-phenanthroline)(η^2-sulfur dioxide)molybdenum(0) (3.534 Å),[49] and (2,4,5-trimethylbenzenethiolato)(3,4,7,8-tetramethyl-1,10-phenanthroline)-copper(I) acetone solvate (3.686 Å).[50]

From the statistical evaluation of the CSD search it becomes evident that a near face-to-face π-stacking interaction is a rare phenomenon. Usually the π-ring planes overlap in an offset or displaced geometry as depicted in Figs. 1, 3 or in **C**. Such a parallel-displaced structure also has a contribution from π–σ

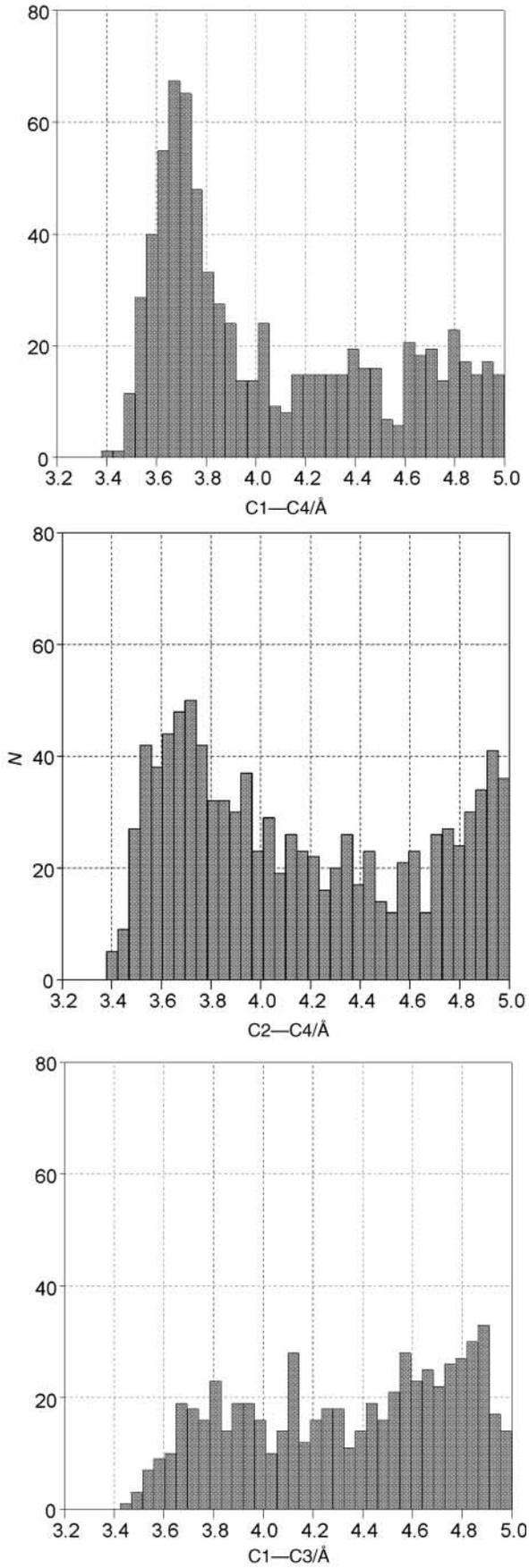


Fig. 11 Histograms for the three different centroid–centroid distances (C*i*–C*j*) between two quinoline–metal fragments from a CSD search as outlined in Fig. 6. C1–C4 is the pyridine–arene-type contact, C2–C4 the arene–arene-type approach, C1–C3 the pyridine–pyridine-type contact. The overall distance between the two quinoline centers was constrained to an *inter*molecular (group) contact between 3.0 and 5.0 Å for the search.

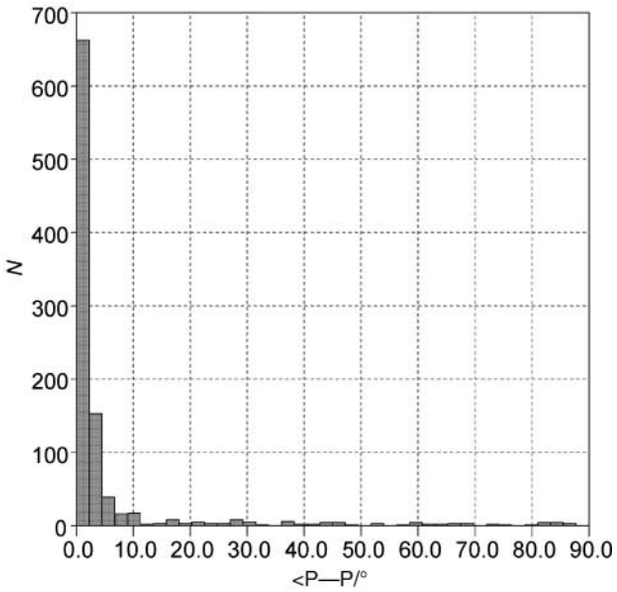


Fig. 12 Histogram for the plane–plane angle between two quinoline-metal fragments from a CSD search as outlined in Fig. 6.

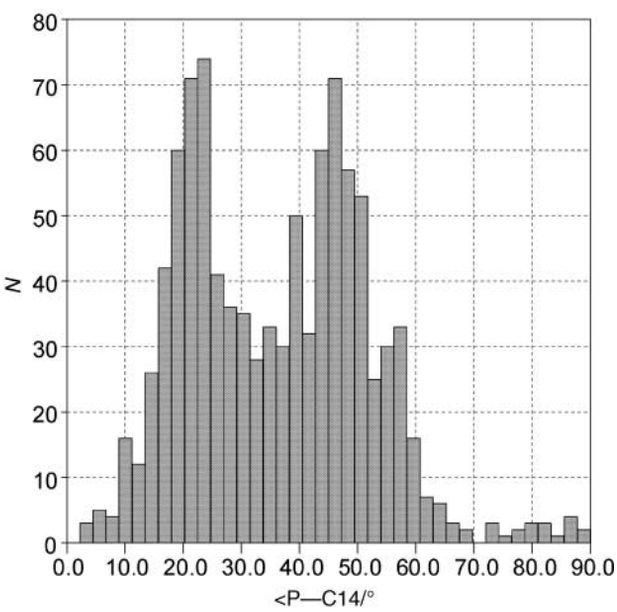


Fig. 13 Histogram for the displacement angle P–C14 defined as the angle between the pyridine–arene ring-centroid vector (C1–C4) and the ring normal to one of the quinoline planes. For further details see caption to Fig. 6. The second maximum around 45° originates when either the two arene or the two pyridine ring sections are in close contact.

attraction (*cf.* Fig. 3), the more so with increasing offset. From the CSD search it was not obvious though if π–π stacking interactions were indeed invoked to discuss and explain the crystal packing. Yet, in the recent literature π–π stacking interactions, justified or not, appear to be used favorably in the discussion of packing phenomena.

Individual examples

In the following are collected a cross-section of metal–ligand compounds where π–π interactions were explicitly pointed out in recent literature entries. The subject does not lend itself to a complete coverage [51] but the examples given here should be representative of how π–π stacking is invoked in metal complexes with nitrogen-containing aromatic ligands.[52] The reader may then judge if such an assignment is correct.

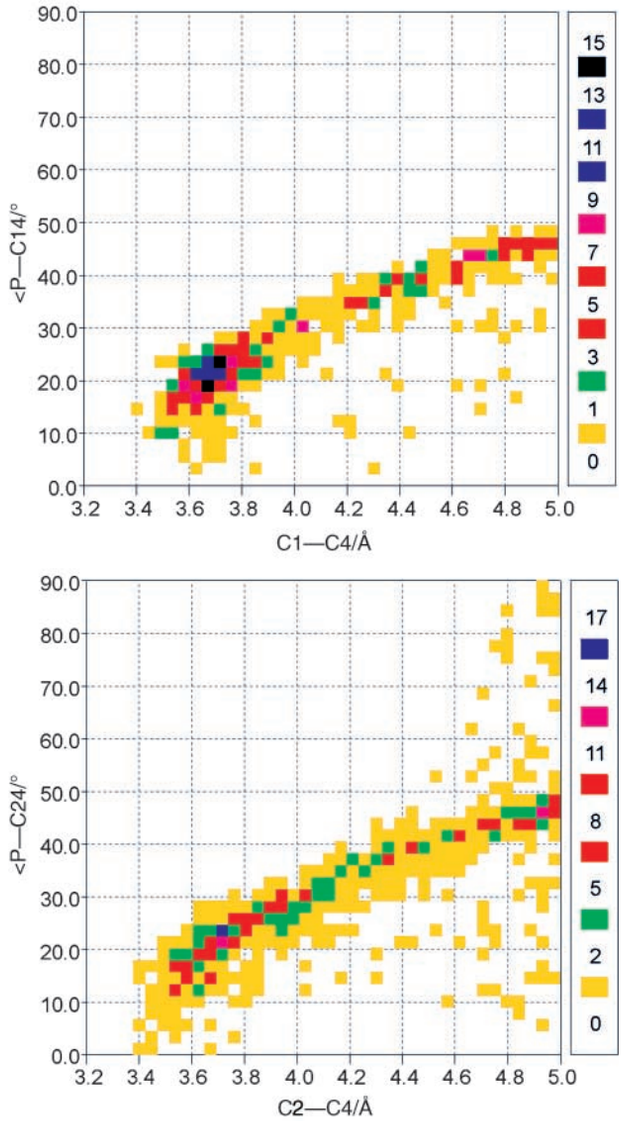


Fig. 14 Scattergrams for a correlation between the displacement angle (P–C*ij*) and the centroid–centroid distance (C*i*–C*j*). C1–C4 is the pyridine–arene-type contact, C2–C4 the arene–arene-type approach. For further details of the CSD search see also Fig. 6.

It is the intention geometrically to assess the overlap of the aromatic rings within the noted π stacking. In the following pictorial illustrations a view direction perpendicular to the π planes was chosen in order best to visualize the relative orientation and overlap of the plane areas. The aromatic ring planes can be assumed parallel to each other within a few degrees unless noted otherwise. The contacts given refer to atom–atom distances of the aromatic rings. The pictures were constructed using the electronic cif files given as supplementary material.[53] The following examples are grouped according to the ligand motif but other classification schemes may have been chosen as well.

The distances of the π–π planes or of the atoms involved are, of course, an important criterion to suggest π stacking in the first place. Usually the interplanar distance is given. However, it is felt that the atom–atom contacts provide for a better criterion in the case of ring slippage and/or ring tilt. Strong interactions are around 3.3 Å and weaker interactions lie above 3.6 Å with 3.8 Å being approximately the maximum contact for which π–π interactions are accepted. It is evident that other packing criteria can easily influence the magnitude of π–π interaction which is one of the weakest interatomic forces. This being the case the shortest distances are listed in the following examples but without detailed discussion.

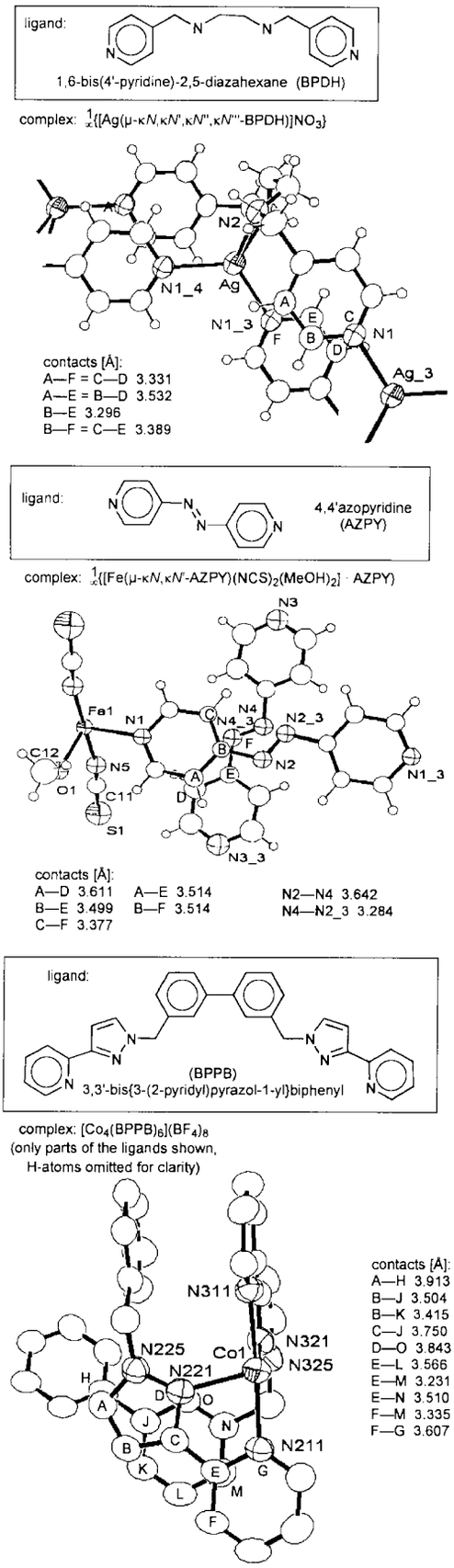


Fig. 15 π–π Interactions in selected complexes with pyridine-based ligands. Sources: $[Ag(BPDH)]NO_3$,[56] $[Fe(AZPY)(NCS)_2(MeOH)_2]\cdot AZPY$,[54] BPPB complexes.[58]

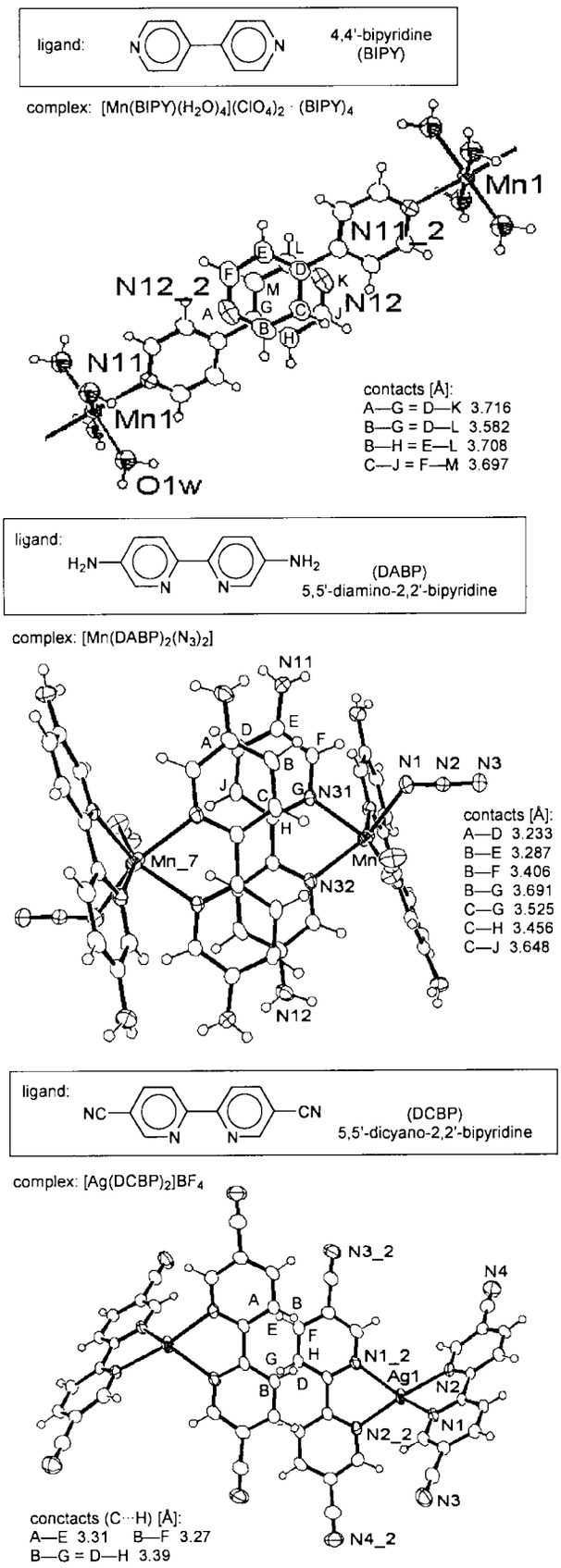


Fig. 16 π–π Interactions in selected complexes with bipyridine-based ligands. Sources: $[Mn(BIPY)(H_2O)_4][ClO_4]_2\cdot 4BIPY$,[55] $[Mn(DABP)_2(N_3)_2]$,[59] $[Ag(DCBP)_2]BF_4$.[57]

Pyridine- and bipyridine-based ligands

A sizable number of ligands used for the construction of coordination polymers is based on pyridine rings. 4,4′-Bipyridine and 2,2′-bipyridine are abundant building blocks. Their importance is reflected in the examples shown in Figs. 15 and 16. The ligands involve to a large extent functionally substituted pyridine and bipyridine groups.

It is evident that the ring–ring area overlap is rather small in most examples from Figs. 15 and 16. An exception is the 4,4′-bipyridine ligand which comes nearer to a face-to-face π-stacked arrangement.[54,55] The pyridine rings of the other ligands interact in an offset or parallel displaced mode. The ring slippage can be quite significant, to the extent that only the edges of the parallel rings are in contact to each other, *e.g.* in the BPDH compounds[56] and in $[Ag(DCBP)_2]BF_4$.[57] Of importance can also be the concomitant interaction of the aromatic ring with the p and π orbital containing functional groups on the aromatic core. Examples are the close contacts with the azo-bridge in the AZPY compound,[54] with the pyrazolyl moiety in the BPPB complexes,[58] with the NH_2 group in a DABP complex[59] (not shown here) and the C≡N–ring contact in a polymeric Ag–DCBP compound (not shown).[57]

Terpyridine ligands

Two examples of complexes with the terpyridine group and noted π–π interaction are collected in Fig. 17. In the complex $[Pt(Ph\text{-}TERPY)Cl]BF_4$ the Pt···Pt contact is the major driving force which brings the ring systems together.[37] In the stacking the complex molecules and the ligands can assume different orientations relative to each other. While the aromatic–aromatic interaction is again offset we note that the conformeric arrangement of $[Pt(Ph\text{-}TERPY)Cl]BF_4$ in Fig. 17 is an example where the nitrogen atoms of the heterocycle come rather close to each other.

With respect to the aromatic interaction in $[\{Ru(TTPY)\}_2(BISTERPY)][PF_6]_4$ the close approach of two carbon atoms to 3.09 Å is due to a tilt of the respective ring planes of 30.8°.[60] The approach is between the N11 ring and the middle pyridyl ring of the TTPY ligand. This is an aromatic interaction which is intermediate between a slipped π stacking and an edge-on C–H···π interaction. Other cases for this kind of intermediate interaction were observed in complexes with the hydrotris(indazolyl)borato ligand (not detailed here).[21]

Heterocycles with two nitrogen atoms: pyrimidine and bipyrimidine

The gold complex with the pyrimidinethiolate ligand is another example for a near face-to-face π-stacked arrangement (Fig. 18). The π stacking was viewed as remarkable since, unlike in the above platinum-stacks, the Au···Au separation (3.54 and 3.78 Å) is considerably longer than usual aurophilic interactions (3.0–3.2 Å).[39] The bipyrimidine complex shows an offset overlap (Fig. 18).[61]

Heterocycles with extended π systems, anellated aromatic rings: phenanthroline, naphthyridine, *etc.*

Figs. 19 and 20 show examples of complexes whose ligands possess extended π systems through the anellation of aromatic rings. The actual ligands are 4,7-phenanthroline, dipyridophenazine, 2,2′-bi-1,6-naphthyridine and diazafluorenone thiosemicarbazone. From aromatic hydrocarbon structures it is well known that π–π stacking becomes increasingly favorable with the number of connected (anellated) arene rings.[32] Extended ring systems such as pyrene or coronene show an offset π stacking with the hydrogens roughly over ring centers.[14,27,33]

In the complex $^1_\infty[Cu(PHEN)(MeCN)]BF_4$[62] the π–π interaction with its displacement is similar to those of extended aromatic hydrocarbons. The dipyridophenazine–platinum complex $[Pt(DPP)Cl_2]$[63] has been studied as a metallointercalator for DNA through the π interaction between the ligand and the DNA base pairs.[64] The two-dimensional co-ordination polymers of $^2_\infty[M(\mu\text{-}BNP)_2(NCS)_2]$ (M = Co, Zn or Cd) show

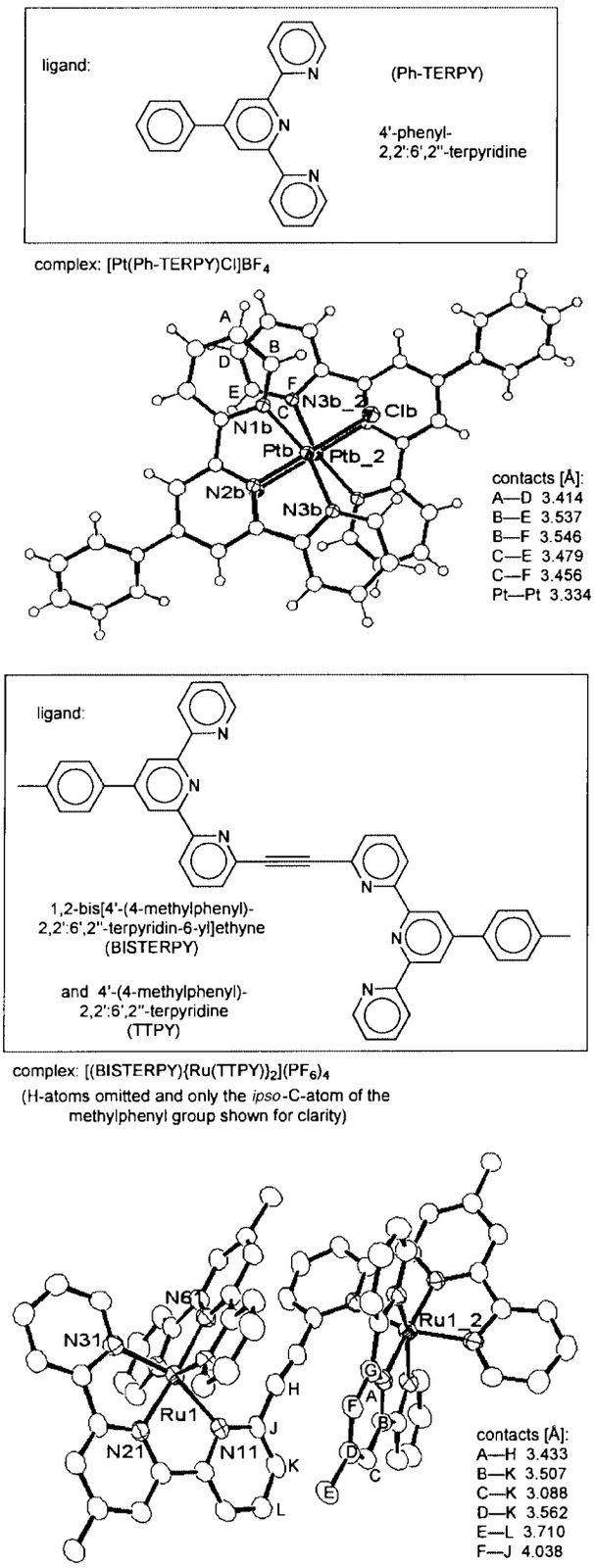


Fig. 17 π–π Interactions in complexes with a terpyridine ligand. Sources: $[Pt(Ph\text{-}TERPY)Cl]BF_4$,[37] $[\{Ru(TTPY)\}_2(BISTERPY)][PF_6]_4$.[60]

the phenomenon of interpenetration and it may be assumed that the non-covalent π–π interactions play an important role for the ligand orientation during the crystallization process.[65] The complex $[Pd(DAFT)_2]$ is somewhat peculiar here, because the diazafluorenone moiety does not bind through its nitrogen donors to the metal. Rather, the metal is co-ordinated by the thiosemicarbazone substituent.[66] Yet, the ligation brings the

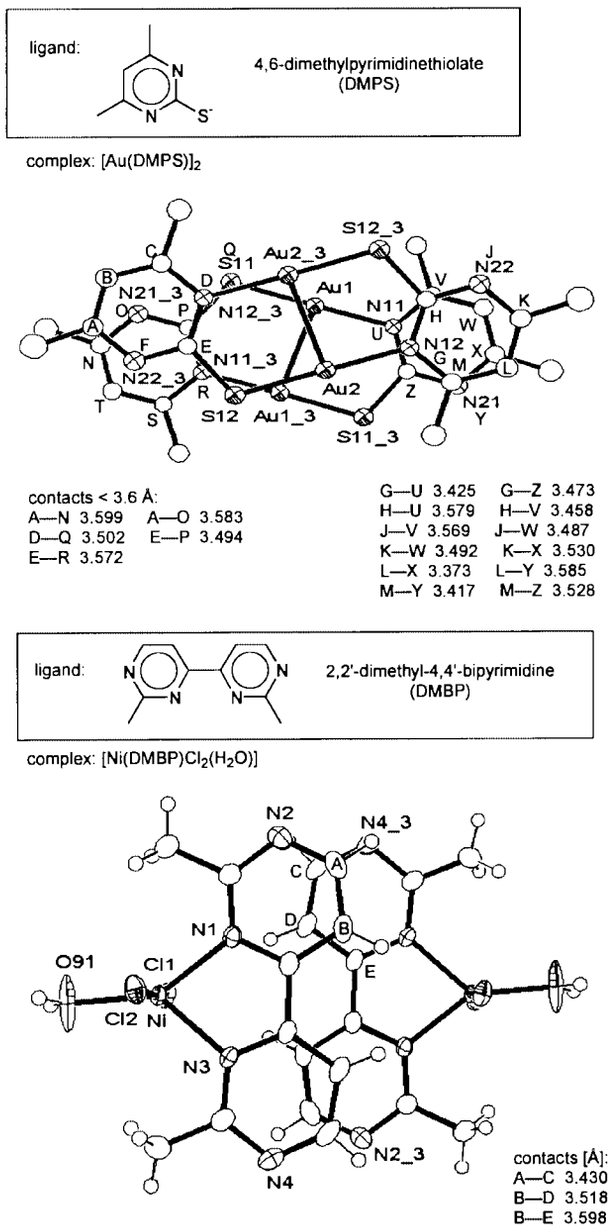


Fig. 18 π–π Interactions in complexes with a pyrimidine ligand. Sources: $[Au(DMPS)]_2$,[39] $[Ni(DMBP)Cl_2(H_2O)]$.[61]

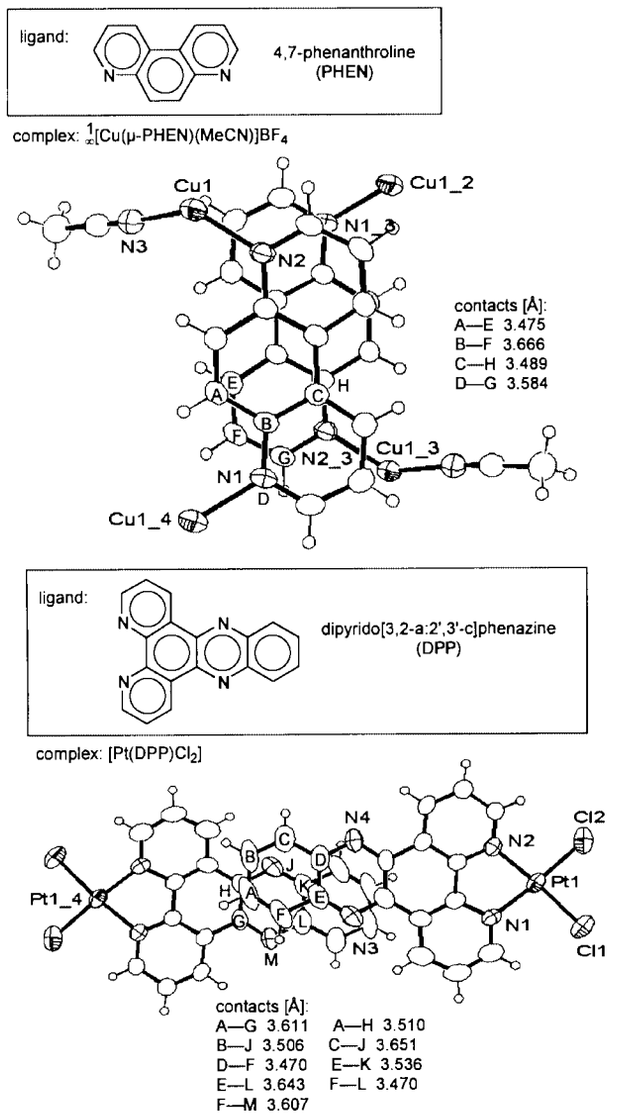


Fig. 19 π–π Interactions in complexes with extended nitrogen-containing aromatic ligands. Sources: PHEN compound,[62] DPP complex.[63]

diazafluorenone groups in close vicinity so that very short intramolecular π–π contacts result.

The extended nitrogen-heterocyclic π systems in Fig. 19 still feature an offset stacking. The extended nature of the π system leads to an increased overlap of the aromatic surface area. It is noteworthy that the shortest contacts among the examples given here are found for compounds with large π systems. The trend observed in aromatic hydrocarbons that π stacking becomes more favorable with increased ring numbers is also well reflected in the nitrogen heterocyclic ligands.

Conclusion

π–π Interactions can play an important role in controlling the packing or assembly of compounds. In many structural descriptions of metal–ligand complexes π–π stacking is invoked as a motif, often without much detail. An analysis of complexes with aromatic nitrogen heterocycles as ligands reveals that such a π–π stacking is usually an offset or slipped facial arrangement of the rings. A near face-to-face alignment of the rings is extremely rare. The usual π interaction is an offset or slipped stacking, *i.e.* the rings are parallel displaced. The ring normal and the vector between the ring centroids form an angle of about 20° up to centroid–centroid distances of 3.8 Å. Such a parallel-displaced structure also has a contribution from π–σ attraction, the more so with increasing offset. Only a limited number of structures with a near to perfect facial alignment exists. The assessed examples had a ring-plane overlap below 30% of the ring areas. In some cases π–π stacking is often merely an overlayering at the edges of the rings. Then, the interaction is probably more of a C–H · · · π type and driven by the known π–σ attraction. The rings of stacked extended π systems are still displaced with respect to each other. From the extended nature of the π system results, however, an increased overlap of the aromatic surface areas. The heterocyclic rings mostly overlap with their carbon atoms, followed by carbon–nitrogen contacts. An overlap of the nitrogen heteroatoms is also possible but observed less often. For the most part, this atom matching may be dictated by the occupation of the nitrogen atoms in co-ordinative bonding and the geometric constraints imposed thereby. However, it also follows the trend for a preferable overlap of regions with expected low π-electron density according to the Hunter–Sanders rules.

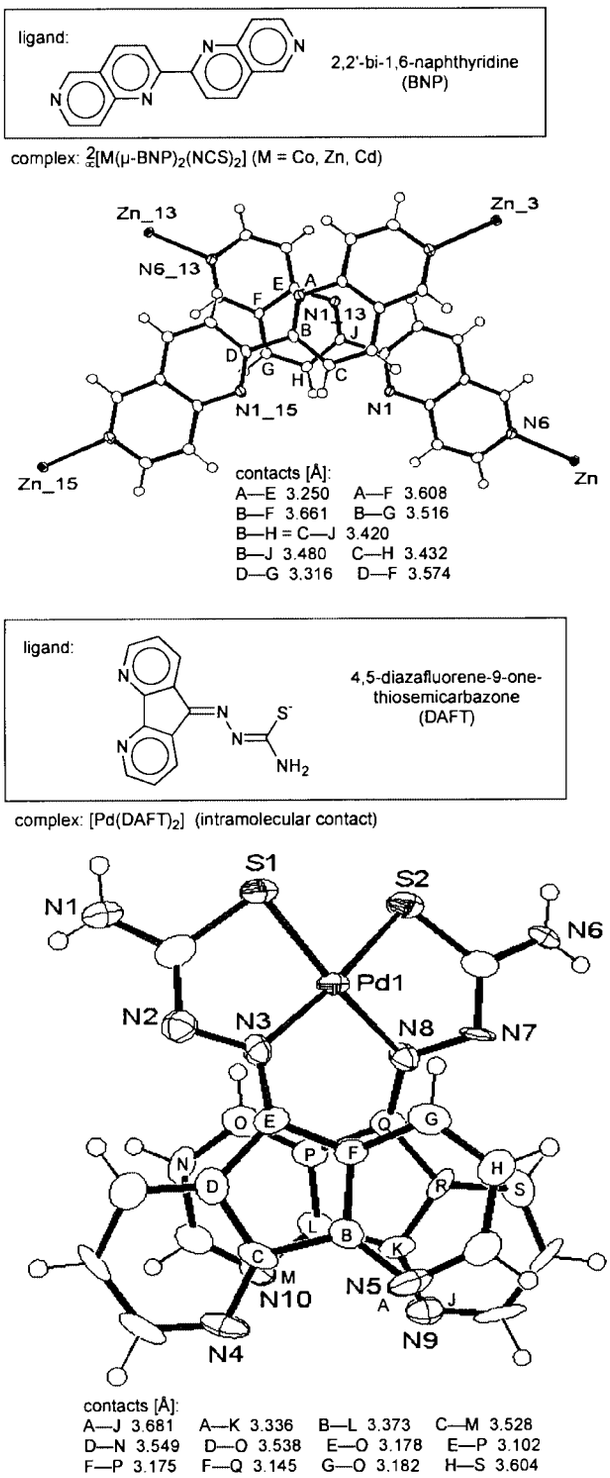


Fig. 20 π–π Interactions in complexes with extended nitrogen-containing aromatic ligands. Sources: BNP compound,[65] DAFT complex.[66]

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (grant Ja466/10-1) and the Fonds der Chemischen Industrie.

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