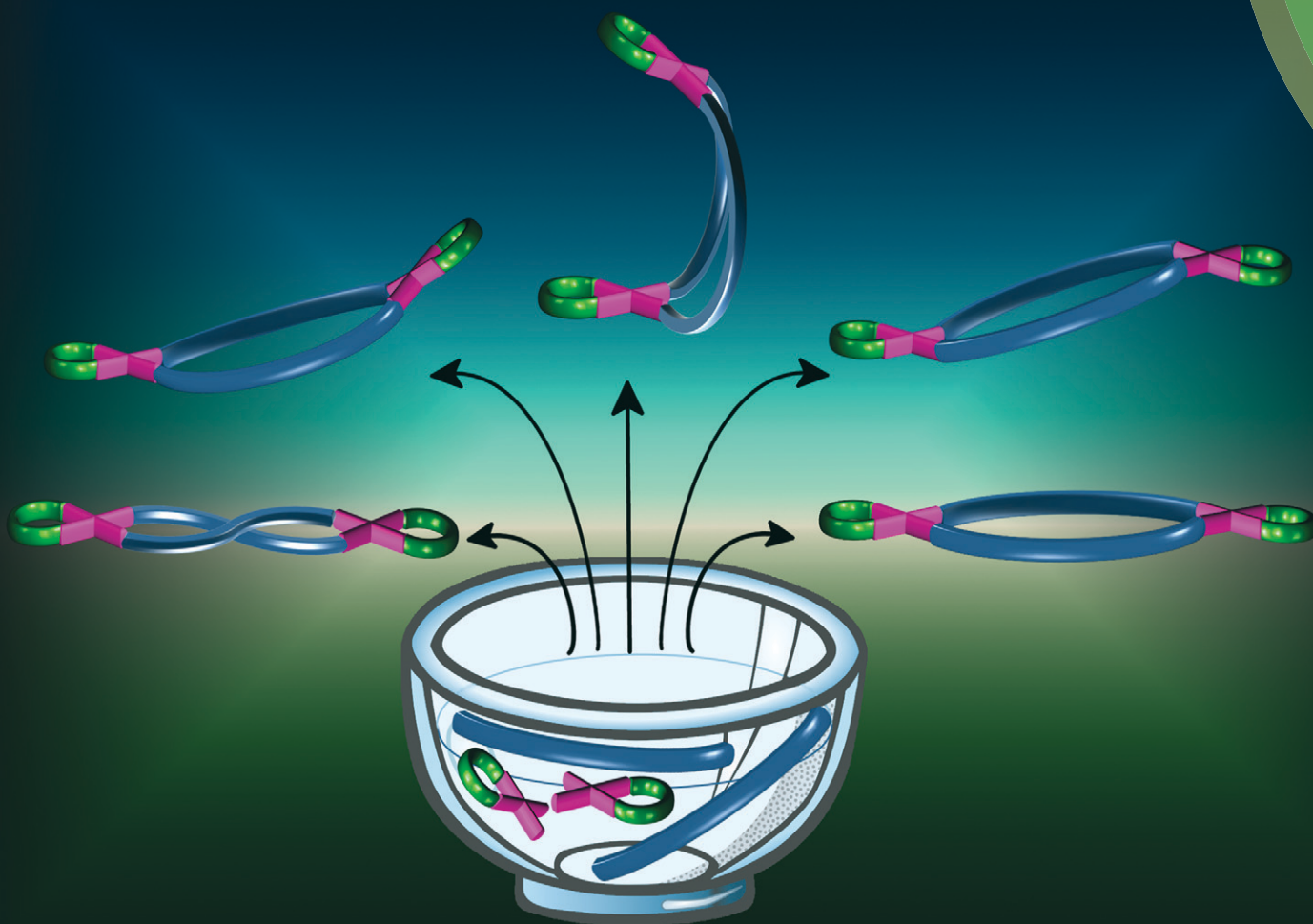


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## HIGHLIGHT

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*cis*-Protected palladium(II) based binuclear complexes as tectons in crystal engineering and the imperative role of the *cis*-protecting agent



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## *cis*-Protected palladium(II) based binuclear complexes as tectons in crystal engineering and the imperative role of the *cis*-protecting agent†

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A survey of the Cambridge Structural Database (CSD) for crystal structures of binuclear coordination complexes, formed by the combination of suitable ligand(s) and Pd(II) centres which are protected in a *cis* fashion by 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), tetramethylethylenediamine (tmeda) or ethylenediamine (en), was carried out. The structures of these binuclear complexes could be classified into five different categories – “opened jaws”, “helicate”, “plateau”, “step” and “bow-shaped” based on the relative spatial orientation of the Pd(II) square planes of the cations and the conformation of the ligand(s). Investigation of the molecular packing in these complexes revealed involvement of the *cis*-protected Pd(II) units in the self-assembly of the cations. Cations in the complexes that contained bpy and phen moieties often assembled via  $\pi \cdots \pi$  stacking and C–H $\cdots\pi$  interactions between the aromatic rings of the *cis*-protecting Pd(II) units. In contrast, in the en and tmeda complexes, molecular self-organisation in most cases occurred through noncovalent interactions between the *cis*-protected Pd(II) units and the ligand, counteranion or included solvent molecules. Hence, the cations can be defined as ‘tectons’, each of which contains two *cis*-protecting units, which play the role of ‘supramolecular synthons’ in the self-assembly of these binuclear complexes. The study of these crystal structures provides information about preferred patterns of molecular association in these complexes, which is invaluable for the crystal engineering of pre-designed self-assembled coordination complexes for desired functions or properties.

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## 1. Introduction

Solid-state chemistry deals with the synthesis, characterisation and applications of solid materials. It includes areas of



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study as diverse as materials science, organic chemistry, solid-state physics, inorganic chemistry, physical chemistry, metallurgy and the chemistry of minerals.<sup>1</sup> The solid-state structures and properties of chemical compounds are often different from those observed in the solution state, arising from the packing of the constituent molecules, atoms or ions. Advances in the field of X-ray crystallography have led to the increased availability of modern instruments and software for determining single crystal structures rapidly and accurately, resulting in an upsurge of interest in structural chemistry. Organic chemists have recognised the potential of the crystalline state in recent decades, with numerous literature accounts devoted to understanding phenomena such as polymorphism, solvatomorphism, phase transitions and solid-state reactions. These studies led to the development of the field of crystal engineering which deals with the understanding of intermolecular interactions and their subsequent use in the design and synthesis of molecular solids with desired structures and properties.<sup>2</sup> Molecular subunits termed 'supramolecular synthons' can be reliably utilised to build a structure with the desired molecular organisation, an approach that parallels retrosynthesis in synthetic organic chemistry. In contrast, tectons are molecules that contain information regarding intermolecular recognition, which results in their self-assembly into crystalline networks upon combination with suitable atoms or molecules.<sup>3</sup> For instance, the carboxylic acid dimer and amide synthons are ubiquitous in organic crystal engineering, while 4,4'-bipyridine and related linear linkers are commonly used as tectons in the construction of coordination networks and metallocsupramolecular structures.<sup>4</sup>

Crystal engineering in organic compounds has been the focus of many literature reports, reviews,<sup>5</sup> books<sup>2a,6</sup> and even a textbook.<sup>7</sup> However, the crystal structures of metal-organic compounds have not received as much attention, apart from coordination polymers and metal organic frameworks.<sup>8</sup> Robson and Hoskins described the metal atom as a node and the coordinated ligand as a connector or linker in their report of the crystal structure of zinc cyanide, setting the stage for crystal engineering in coordination polymers.<sup>9</sup> Since then, the field has grown rapidly, with the synthesised networks finding applications as NLO materials,<sup>10</sup> materials for gas adsorption and storage<sup>11</sup> and catalysis,<sup>12</sup> as chemical sensors<sup>13</sup> and as substrates for solid-state reactions.<sup>14</sup>

Transition metal ions provide a wide range of coordination geometries upon complexation, which can be exploited for preparing a variety of discrete complexes or polymeric networks. There are several literature reports describing the formation of pre-designed coordination complexes obtained by judiciously choosing ligands and metal ions.<sup>15</sup> However, studies of noncovalent interactions involving specific molecular sub-units in the complexes that contribute to different modes of molecular organisation in the solid-state, are less common. This information can provide insight into the role of intermolecular interactions in the structures of functional coordination complexes, aiding in the design of crystalline metal-organic solids with desired molecular packing and in

the modification of their solid-state properties.<sup>16</sup> In general, it is observed that the hydrogen bonding patterns associated with common functional groups in organic crystals are also seen in the crystal structures of metal-organic compounds,<sup>17</sup> leading to their use as supramolecular synthons in the crystal engineering of coordination complexes. Despite the availability of this information at the disposal of the solid-state chemist, crystalline forms different from those desired or envisaged are often obtained during crystallisation. They appear concomitantly with the required crystals in the form of polymorphs or solvates (formed by the mediation of solvents during crystallisation). In coordination complexes, counteranions or solvents in the crystal lattice often influence hydrogen bonding outcomes and the molecular packing, in addition to the occurrence of phenomena such as supramolecular isomerism.<sup>18</sup>

## 2. Background

The Cambridge Structural Database<sup>19</sup> (CSD, version 5.36, with updates to May 2015) contains 758 844 structures out of which 323 149 are organic structures (42%) while more than 375 561 (49%) contain at least one transition metal. Of these, a total of 37 731 structures (10%) contain either Pd (19 632 structures) or Pt (18 099 structures) atoms. The Pd(II) metal centre has been exploited for the design and preparation of various self-assembled coordination compounds, particularly because of its ability to form discrete and stable square planar complexes. The added advantage of using Pd(II) is the favourable dynamic nature of the metal-ligand interaction, which is indispensable for the self-healing of wrongly formed structures, and leads to the formation of a thermodynamically stable equilibrium.<sup>15b,20</sup>

In our laboratory, we synthesised a series of pre-designed Pd(II) based self-assembled coordination compounds by combining selected nonchelating ligands with *cis*-protected metal centres. We determined the crystal structures of *cis*-protected Pd(II) based binuclear complexes containing pyridyl N-donor ligands with urea,<sup>21</sup> piperazine<sup>22</sup> and imidazole cores.<sup>23</sup> The effect of changing the *cis*-protected Pd(II) unit on the structure and molecular packing of these self-assembled complexes prompted a survey of the CSD for the structures of similar complexes. We present some of our results here along with comparisons of the structures available in the CSD.

The complexation of *cis*-protected Pd(II) units (Pd(L')) with chosen ligand(s) (L) results in discrete Pd<sub>x</sub>L'<sub>x</sub>L<sub>y</sub> type coordination complexes, where the ratio and values of 'x' and 'y' depend upon the denticity of the ligand(s) and the direction of coordination vectors, respectively. The general molecular formula of the complex is represented as [Pd<sub>x</sub>(L')<sub>x</sub>(L)<sub>y</sub>](monoanion)<sub>2x</sub>. In this formula, L' denotes a chelating bidentate ligand, *i.e.*, ethylenediamine (en), tetramethylethylenediamine (tmeda), 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen). The nonchelating ligand(s), L, often contains N-donor atoms (belonging to pyridine rings) and may also be a metalloligand with the metal centre in most

cases being Pt(II). A discrete structure is obtained in most of the designs, whereas, a dynamic equilibrium containing two or more species is observed in some cases. For instance, mixtures of mononuclear and binuclear,<sup>24</sup> binuclear and trinuclear,<sup>25</sup> or trinuclear and tetranuclear complexes<sup>26</sup> have been reported. A few examples of ligands that form coordination polymers when combined with *cis*-protected Pd(II) units are also reported.<sup>27</sup> In this review, we present the analysis and comparison of related structures of complexes containing two *cis*-protected Pd(II) units, designated as binuclear complexes. Other metal atoms may be present in the structure (ligand moiety) if the coordinating ligand is a metalloligand.

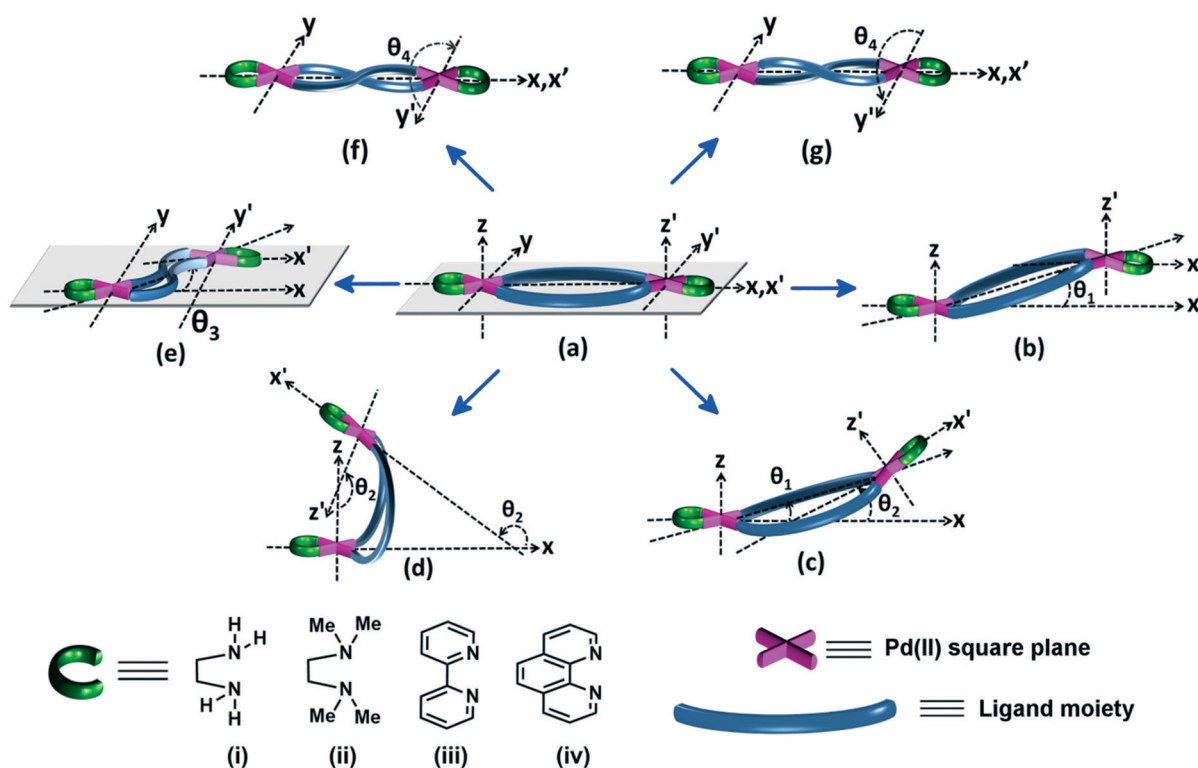
### 3. Methodology

A survey of the CSD<sup>19</sup> was undertaken for examining the crystal structures of *cis*-protected Pd(II) based binuclear complexes. We searched for structures containing [Pd(en)]<sup>2+</sup>, [Pd(tmeda)]<sup>2+</sup>, [Pd(bpy)]<sup>2+</sup> and [Pd(phen)]<sup>2+</sup> moieties, in turn, with no restrictions on the ligand(s) coordinated to the Pd(II) metal centre or counteranions. Structures which showed disorder in the main cationic unit were not considered further for analysis. The structures were sorted manually into categories based on the *cis*-protected Pd(II) unit and the relative orientation of the Pd–(N)<sub>2</sub>(X)<sub>2</sub> planes, where N and X (usually N/S/O/C) represent the donor atoms of the *cis*-protecting unit

and the chosen ligand, respectively. The different modes of packing of the cationic units in the crystal structures of these self-assembled complexes were analysed in the context of the role played by the *cis*-protecting agent in the molecular self-assembly. The imperative role of the *cis*-protecting units containing  $\pi$ -surfaces in steering the packing of the cations was observed and is discussed in the following sections.

### 4. Classification of binuclear complexes

Binuclear complexes may be formed by the combination of two units of selected *cis*-protected Pd(II) centres Pd(L') with: (a) two units of a bidentate ligand L<sup>B</sup>, *i.e.* [Pd<sub>2</sub>(L')<sub>2</sub>(L<sup>B</sup>)<sub>2</sub>], (b) one unit each of two different bidentate ligands L<sup>B1</sup> and L<sup>B2</sup>, *i.e.* [Pd<sub>2</sub>(L')<sub>2</sub>(L<sup>B1</sup>)(L<sup>B2</sup>)], (c) one unit of a bidentate ligand L<sup>B</sup> and two units of a monodentate ligand L<sup>M</sup>, *i.e.* [Pd<sub>2</sub>(L')<sub>2</sub>(L<sup>B</sup>)(L<sup>M</sup>)<sub>2</sub>], (d) one unit of a bis-chelating tetradentate ligand L<sup>Q</sup>, *i.e.* [Pd<sub>2</sub>(L')<sub>2</sub>(L<sup>Q</sup>)] or (e) one unit each of a tridentate ligand L<sup>T</sup> and a monodentate ligand L<sup>M</sup>, *i.e.* [Pd<sub>2</sub>(L')<sub>2</sub>(L<sup>T</sup>)(L<sup>M</sup>)], the first category accounting for the largest number of examples. As shown in Fig. 1, the approximate shapes of various *cis*-[Pd<sub>2</sub>(L')<sub>2</sub>(L<sup>B</sup>)<sub>2</sub>] type molecules, derived by displacement of one of the Pd–(N)<sub>2</sub>(X)<sub>2</sub> planes, while keeping the other plane at a fixed position are: (a) “plateau” (no displacement); (b) “step” (axially displaced from plateau by an acute angle  $\theta_1$ ); (c)



**Fig. 1** Schematic depiction of coordination complexes of Pd<sub>2</sub>(L')<sub>2</sub>(L<sup>B</sup>)<sub>2</sub> formulation showing the spatial orientation of ligands and relative positions of the two Pd–(N)<sub>2</sub>(X)<sub>2</sub> square planes in a variety of architectures: (a) “plateau”, (b) “step”, (c) “bow-shaped”, (d) “opened jaws”, (e) “zigzag plateau”, and (f) and (g) left-handed (M, or minus) and right-handed (P, or plus) “helicates”, respectively, derived from “plateau” (adapted from ref. 23 reprinted with permission from M. C. Naranthatta, S. Bandi, R. Jagan, and D. K. Chand, *Cryst. Growth Des.*, 2016, 16, 6722. © 2016 American Chemical Society). The “twisted” Pd<sub>2</sub>(L')<sub>2</sub>(L<sup>Q</sup>) type complexes are depicted in Fig. 7.

“bow-shaped” (radially displaced from plateau by an acute angle  $\theta_2$ ); (d) “opened jaws” (radially displaced from plateau by an obtuse angle  $\theta_2$ ); (e) “zigzag plateau” (displacement from “plateau” in the  $xy$ -plane by an acute angle  $\theta_3$ ) and (f), (g) left-handed and right-handed “helicate” (circularly displaced from “plateau” in either direction by  $\theta_4$ ). A variant of the “helicate” is the “twisted” architecture, which comprises a single tetradentate ligand coordinated to two *cis*-protected Pd(II) centres with the two Pd–(N)<sub>2</sub>(X)<sub>2</sub> planes oriented nearly perpendicular to each other. The “opened jaws”, “step” and “plateau” architectures are common, whereas the “bow” and “zigzag plateau” shapes are seldom observed (Fig. 1). A plot of the number of structures vs. the type of assembly shows the distribution of the various types across the four *cis*-protected Pd(II) units (Fig. 2). For clarity and simplicity, the formula [Pd<sub>2</sub>(L')<sub>2</sub>(L<sup>B</sup>)<sub>2</sub>] and its corresponding schematic diagram (Fig. 1) are used here to represent the binuclear complex. The relative positions of the two Pd–(N)<sub>2</sub>(X)<sub>2</sub> square planes in a [Pd<sub>2</sub>(L')<sub>2</sub>(L<sup>B</sup>)<sub>2</sub>] structure depend upon the spatial positions of the coordination vectors of the nonchelating bidentate ligand component.

The largest number of structures belong to the “opened jaws” category (Table S1†), followed by “step”, “plateau”, “helicate” and “bow” (Tables S2–S5†). Structures containing en and tmeda are distributed across all types, but many belong to the “opened jaws”, “plateau” or “step” category. The  $\theta_1$  values (Fig. 1b) for a few structures of the “step” type lie in the range of 0–1°, particularly when the *cis*-protecting unit is en, blurring the line between the “plateau” and “step” types of assemblies (Tables S3 and S4†). These examples have been placed in the “plateau” category. Complexes of the “zigzag plateau” and “twisted” types are placed in the “plateau” and

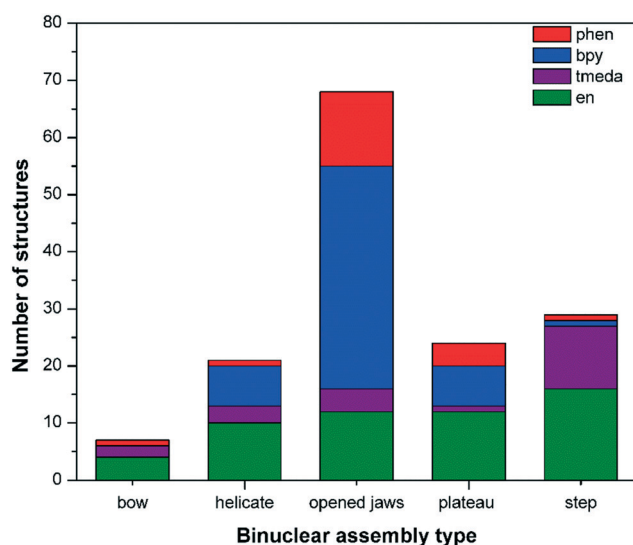


Fig. 2 Plot of the number of structures (irrespective of the number and denticity of the ligand(s) coordinated to Pd(II)) vs. the binuclear assembly type shows distribution of the various types of complexes across the four *cis*-protected Pd(II) units. “Zigzag plateau” and “twisted” types are placed in the “plateau” and “helicate” categories, respectively.

“helicate” categories, respectively. In a few examples of the “opened jaws” and “twisted” categories, the second Pd–(N)<sub>2</sub>(X)<sub>2</sub> plane lies slightly displaced from the ideal positions described in Fig. 1. Incidentally, the helicate type complexes are the rarest when the “twisted” type is not counted.

Each structure has been assigned a number (see Table 1, Tables S1–S5†) and is also identified by its CSD refcode. Representative examples for each type of packing are discussed in the sections below and molecular packing diagrams for all structures are available in the ESI.†

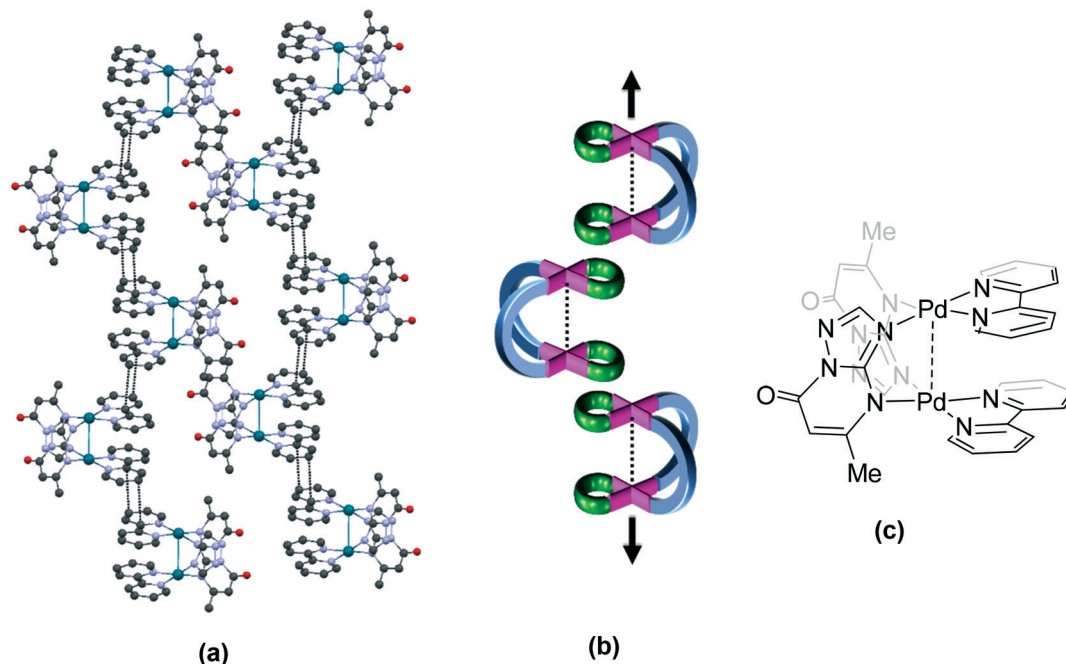
#### 4.1. “Opened jaws”

The solid-state conformation of the molecule in many examples in the “opened jaws” category is driven by intra/inter molecular  $\pi\cdots\pi$  stacking interactions and/or intramolecular metal–metal interactions.<sup>28</sup> The intramolecular Pd $\cdots$ Pd distances<sup>29</sup> in most of the “opened jaws” structures containing bpy and phen lie in the range of 2.7–3.7 Å (and exhibit intramolecular metal $\cdots$ metal interactions), whereas, those which contain tmeda and en often exhibit larger Pd $\cdots$ Pd distances in their structures (Table S1†). This structural variation can be attributed to the fact that structures containing bpy or phen units are also likely to exhibit intramolecular  $\pi\cdots\pi$  stacking interactions<sup>30</sup> between the aromatic rings of the bipyridine or phenanthroline units. Accordingly, the intramolecular Pd $\cdots$ Pd distances are defined as ‘short’ (2.7–3.7 Å) or ‘long’ (>4.0 Å) in these complexes (Table S1†) with there being no examples with the Pd $\cdots$ Pd distance in the range of 3.7–4.0 Å. The types of molecular packing adopted by the cations in these complexes may be broadly divided into four categories. In the case of complexes with ‘short’ intramolecular Pd $\cdots$ Pd distances, cations may associate directly *via* Pd $\cdots$ Pd interactions and/or  $\pi\cdots\pi$  stacking interactions (bpy/phen units) and form infinitely long columns (Fig. 3b) or dimers (Fig. 4b), which may be further linked by anions or solvent molecules. With increasing Pd $\cdots$ Pd distance, a cavity is created between the “opened jaws”, which may be occupied by anions or solvent molecules (Fig. 5b). However, one or more *cis*-protected Pd(II) units may also be partially accommodated in the cavity, resulting in a closed packed structure (Fig. 6b). Illustrative examples of each type of packing are discussed below, along with related structures.

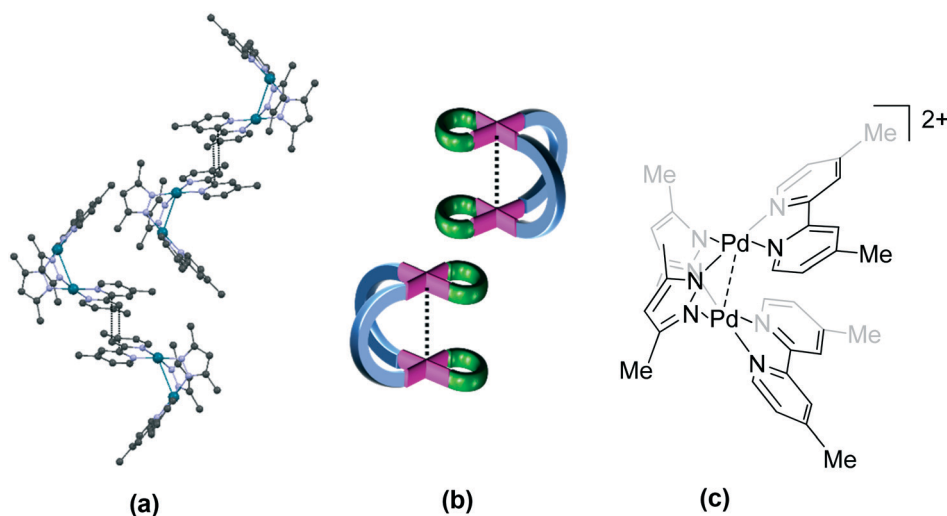
**4.1.1. Complexes with short intramolecular Pd $\cdots$ Pd distances (2.7–3.7 Å).** Adjacent cationic units in the crystals of 18 (RIZKUG),<sup>31</sup> which contains a substituted pyrimidine ligand, associate *via*  $\pi\cdots\pi$  stacking interactions between the

Table 1 Summary of structure numbers for different architectures

Architecture of the binuclear complexes	Structure number corresponding to the <i>cis</i> -protecting units:			
	bpy	phen	en	tmeda
“opened jaws”	1–38	39–51	52–62	63–66
“helicate”/“twisted”	67–73	74	75–84	85–87
“plateau”/“zigzag plateau”	88–94	95–98	99–110	111–112
“step”	113	114	115–130	131–141
“bow”	—	142	143–145, 108	146–147



**Fig. 3** Association of cationic units in (a) **18** (RIZKUG)<sup>31</sup> through  $\pi\cdots\pi$  stacking interactions between bpy units forming a column-like assembly; (b) its schematic representation and (c) the chemical structure of the cationic unit in **18**. Some anions, solvent and hydrogen atoms and interactions are omitted for clarity. Dotted lines between Pd atoms indicate metal $\cdots$ metal interaction.



**Fig. 4** Dimeric association of cationic units in (a) **29** (VERRUG)<sup>51</sup> via  $\pi$  stacking interactions between bpy units; (b) its schematic representation and (c) the chemical structure of the cationic unit in **29**. Some anions, solvent and hydrogen atoms and interactions are omitted for clarity. Dotted lines between Pd atoms indicate metal $\cdots$ metal interaction.

aromatic rings of the bpy units, forming infinitely long molecular columns (Fig. 3a). This pattern of molecular packing is observed in the bpy complexes **1** (AGIGAZ),<sup>32</sup> formed with a 2,2'-azanediylidibenzoic dianion as the ligand; **2** (BATMOY),<sup>33</sup> **3** (BATPIV),<sup>33</sup> **5** (FASQUL)<sup>34</sup> and **6** (FASRAS),<sup>34</sup> formed using the related ligands 1,8-naphthyridin-2,7-dione, 7-amino-1,8-naphthyridin-2-one, 1,8-naphthyridin-2-one and 7-methyl-1,8-naphthyridin-2-one, respectively; **14** (NAGSIZ)<sup>35</sup> and **15** (NERHIB),<sup>36</sup> containing chelating bidentate nitrate ligands; **19** (RONQUI),<sup>37</sup> **20** (RONRAP)<sup>37</sup> and **21** (RONRET)<sup>37</sup>

formed using bis-chelating tartrate as the ligand; **27** (SELSUX),<sup>38</sup> formed using the ligand 1-methylthymine; structurally related **31** (WUHCEI)<sup>39</sup> and **32** (WUHCOS)<sup>39</sup> prepared with the ligands 1-methylcytosine and 2-aminopyridine, respectively; **34** (XIMZEZ)<sup>40</sup> formed using acetamide as the ligand and the tris-osmium complex **35** (YUMWEI).<sup>41</sup> The diacetate complex formed by Pd(OAc)<sub>2</sub>(OTf)<sub>2</sub> with neocuproine, **44** (JIWVUH),<sup>42</sup> and the phen complex **42** (JAMLOZ)<sup>43</sup> also exhibit packing of the cationic units in the form of infinitely long molecular columns through  $\pi\cdots\pi$

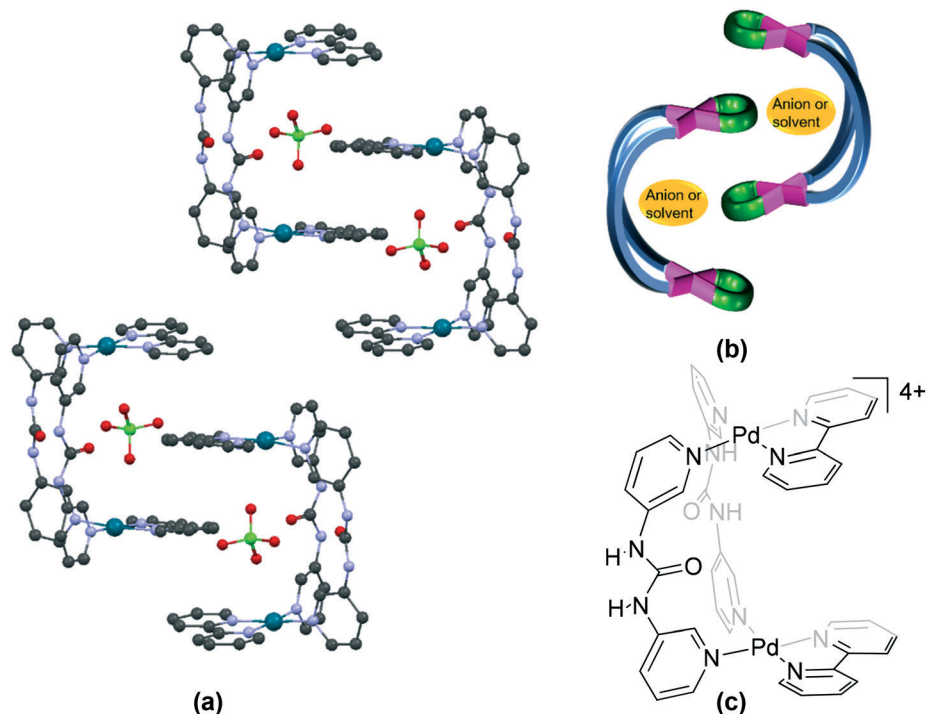


Fig. 5 Self-assembly of molecules in (a) 7 (GEQSEC)<sup>21</sup>; (b) its schematic representation and (c) the chemical structure of the cationic unit in 7. Some anions, solvent and hydrogen atoms and interactions are omitted for clarity.

stacking interactions between the aromatic rings of the phenanthroline moieties.

The bpy complexes 22 (RONRIX)<sup>37</sup> and 33 (XIMZAV)<sup>40</sup> and the bis-acetato and bis-acetamido phen complexes 41 (IVUCIM),<sup>44</sup> 48 (RASZIV)<sup>45</sup> and 49 (RASZOB),<sup>45</sup> respectively,

exhibit a slightly different mode of packing, wherein the cations are alternately linked through Pd···Pd interactions and  $\pi$  stacking interactions, forming columns. In 9 (LABVAN)<sup>46</sup> and 13 (MUBNOM)<sup>47</sup> the cations are packed in infinitely long columns through hydrogen bonding interactions involving the

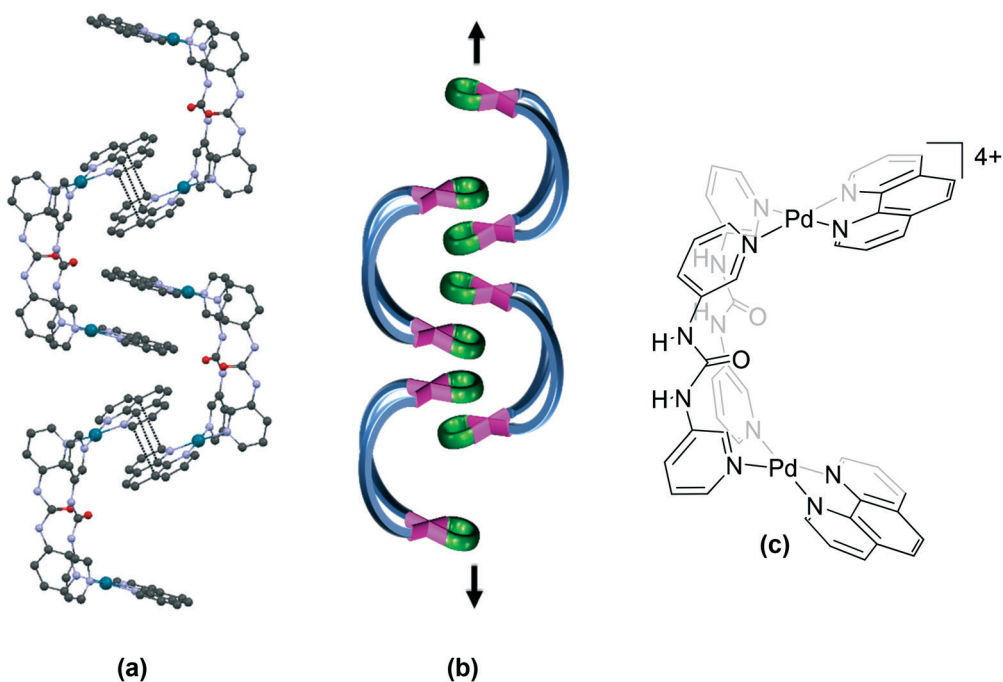


Fig. 6 Association of cations in (a) 40 (GEQSUS)<sup>21</sup>; (b) its schematic representation and (c) the chemical structure of the cationic unit in 40. Some anions, solvent and hydrogen atoms and interactions are omitted for clarity.

atoms of the *cis*-protecting unit and the ligand. The bpy complexes **8** (LABTUF),<sup>46</sup> **12** (MUBNIG)<sup>47</sup> and **23** (RONROD)<sup>37</sup> and the phen complexes **43** (JEGNEP)<sup>48</sup> and **46** (MUBNUS)<sup>47</sup> (with a slightly longer intramolecular Pd···Pd distance) represent structures where the second Pd–(N)<sub>2</sub>(X)<sub>2</sub> is displaced from the ideal position (Fig. 1). The patterns of molecular self-assembly in **8** (LABTUF),<sup>46</sup> **12** (MUBNIG)<sup>47</sup> and **46** (MUBNUS)<sup>47</sup> are like that observed in **18** (RIZKUG)<sup>31</sup> (Fig. 3), *i.e.* formation of infinitely long molecular columns through  $\pi$  stacking interactions. However, in **23** (RONROD)<sup>37</sup> and **43** (JEGNEP),<sup>48</sup> the cations assemble in the form of parallel catemeric chains *via*  $\pi$  stacking interactions. The cations in **62** (XIMZOJ),<sup>40</sup> the en analogue of **33** (XIMZAV),<sup>40</sup> assemble in infinitely long columns through N–H···O interactions between the en unit and ligand, analogous to the molecular assembly through  $\pi$ ··· $\pi$  stacking observed in bpy/phen complexes. The corresponding packing diagrams for these structures are available in the ESI† (Fig. S1–S30).

The tetranuclear [Pd<sub>2</sub>(L')<sub>2</sub>(ML)<sub>2</sub>] (where ML is a metalloligand, M is Pd in this case) “opened jaws” complexes, formed by 2-aminoethanethiolate upon complexation with *cis*-protected Pd(II) units containing bpy (**38**),<sup>49</sup> phen (**50**),<sup>50</sup> dimethyl bpy (**37**),<sup>50</sup> and dimethyl phen (**51**)<sup>50</sup> units, also exhibit short Pd···Pd distances and adopt different modes of molecular packing in the solid state. In **38** (DEBKEA),<sup>49</sup> pairs of molecules associated through  $\pi$ ··· $\pi$  stacking interactions between the bpy units. Anion··· $\pi$  interactions in **38** (DEBKEA)<sup>49</sup> prevent the extension of these dimers into infinitely long molecular columns, unlike the structure of its phen counterpart **50** (XIDSOS).<sup>50</sup> The introduction of a pair of methyl substituents in the aromatic rings results in molecular assembly in the form of columns through  $\pi$ ··· $\pi$  and C–H··· $\pi$  interactions in **37** (XIDSIM)<sup>50</sup> and  $\pi$ ··· $\pi$  stacking in **51** (XIDSUY).<sup>50</sup> These modes of packing can be correlated with those observed in the case of simple binuclear complexes. The corresponding packing diagrams for these structures are available in the ESI† (Fig. S31–S34).

In some of the structures with short Pd···Pd distances, cationic units associate *via*  $\pi$ ··· $\pi$  stacking interactions (in the case of bpy and phen) or Pd···Pd interactions (in the case of en and tmeda) and form dimers. These dimers may be linked by anions or solvent molecules which interrupt further propagation of the cationic assembly. For instance, in **29** (VERRUG),<sup>51</sup> where L is dimethylpyrazole, the cations associate through  $\pi$ ··· $\pi$  stacking interactions between the bpy units, forming dimers (Fig. 4a) which are linked by PF<sub>6</sub> anions (not shown). The cations in the bpy complex **25** (SAZMEN),<sup>52</sup> formed using a pyridinyl dimethylpyrazole ligand, and the phen complex **47** (MULKAF)<sup>53</sup> assemble in this fashion, as well as those in the bpy complexes of the [Pd<sub>2</sub>(L')<sub>2</sub>(L<sup>B</sup>)(L<sup>M</sup>)<sub>2</sub>] variety, **24** (RORFUZ)<sup>54</sup> and **36** (YUPMAY).<sup>55</sup>

The cations in the  $\alpha$ -pyridone complexes **52** (ACIMIJ)<sup>56</sup> and **61** (VENHEB10)<sup>57</sup> containing the counteranions perchlorate and nitrate, respectively, and en as the *cis*-protecting unit, assemble as dimers through intermolecular Pd···Pd interactions and supporting N–H···O and C–H··· $\pi$  interactions

between the ligand and en units. Interestingly, all the tmeda complexes exhibit Pd···Pd distances greater than 4.0 Å (Table S1†). This is perhaps due to the steric aspects associated with the proximity of the methyl groups in an “opened jaws” conformation. The corresponding packing diagrams for these structures are available in the ESI† (Fig. S35–S40).

**4.1.2. Complexes with long intramolecular Pd···Pd distances (>4.0 Å).** Complex **26** (SEHKUN),<sup>58</sup> which contains two *tert*-butyl substituted Pd(bpy)<sup>2+</sup> units coordinated to four pyridine 4-thiol ligands separated by ZnCl<sub>2</sub> spacers and a ‘long’ Pd···Pd distance, reveals packing of the cationic units in the form of infinitely long helical chains through  $\pi$ ··· $\pi$  stacking interactions between the bpy units. The phen complex **39** (EMEHIO)<sup>59</sup> also contains Pd atoms separated by greater than 4.0 Å, wherein the cations assemble to form infinitely long chains *via*  $\pi$ ··· $\pi$  stacking interactions.

This category also contains a family of complexes (bpy – **7** (GEQSEC), phen – **40** (GEQSUS), en – **53** (GEQSIG) and tmeda – **63** (GEQSOM)) formed from the combination of a urea based ligand and the four *cis*-protected Pd(II) units,<sup>21</sup> reported recently from our laboratory.<sup>21</sup> The bpy complex **7** (GEQSEC) shows a completely different type of packing due to the presence of the perchlorate anion in the cavity of the cationic unit (Fig. 5a). The perchlorate forms hydrogen bonding interactions with the urea protons and prevents the close approach of the second cationic unit. The aromatic rings of complexed ligands in adjacent cationic units interact through  $\pi$  stacking interactions. A similar kind of molecular packing is observed in its en and tmeda analogues, **53** (GEQSIG)<sup>21</sup> and **63** (GEQSOM),<sup>21</sup> though the nitrate counteranions in the former structure are not present in the cavity of the “opened jaws”. Further, the introduction of a methyl group in the aromatic ring of the urea based ligand followed by complexation with [Pd(en)(NO<sub>3</sub>)<sub>2</sub>] results in the complex **54** (KAXJOK)<sup>60</sup> with molecular packing like that observed in **63**.

The diphenylpyrazolato bridged bpy and phen complexes **11** (MAQFIU)<sup>61</sup> and **45** (MAQFEQ),<sup>61</sup> respectively, exhibit modes of self-assembly like **7**, even though the intramolecular Pd···Pd distances in the structures are ~3.0 Å. Tetrafluoroborate and nitrate anions, respectively, occupy the cavity created by the “opened jaws”. These complexes also exhibit intramolecular Pd···Pd interactions. The en complex **56** (NEPCER),<sup>25b</sup> containing a bis-pyridyl benzene ligand, can also be classified in this category, with nitrates occupying the cavity of the cationic unit. In the [Pd<sub>2</sub>(L')<sub>2</sub>(L<sup>Q</sup>)] tmeda complex **66** (SUHFUX),<sup>62</sup> the anions do not occupy the cavity of the displaced “opened jaws”. However, the packing of the cations is like that observed in **7**.<sup>21</sup> The corresponding packing diagrams for these structures are available in the ESI† (Fig. S41–S49).

A fourth type of molecular packing in “opened jaws” complexes is seen in the crystal structure of **40** (GEQSUS).<sup>21</sup> The cationic units in the phen complex associate through  $\pi$  stacking interactions between the aromatic rings of the *cis*-protected Pd(II) unit, resulting in two *cis*-protected metal centres, one each from two different molecules accommodated in the cavity of a third molecule (Fig. 6a).





Fig. 7 Schematic representation of (a) a "helicite" complex formed from two bidentate ligands and (b) a "twisted" complex formed from one unit of a tetradentate ligand.

Apart from the four types of molecular packing discussed here, some "opened jaws" complexes exhibit other modes of organization in the solid state. These structures cannot be readily classified into different categories and hence, their packing diagrams are placed in the ESI† (Fig. S50–S62). They include the bpy complexes 4 (EDUSIG),<sup>63</sup> 10 (LAJVOH),<sup>64</sup> 16 (PEYBOL),<sup>65</sup> 17 (POZGEQ),<sup>66</sup> 28 (SOSQUO)<sup>67</sup> and 30 (VIDJAU),<sup>68</sup> the en complexes 55 (LABDAU),<sup>69</sup> 57 (RIZKOA),<sup>31</sup> 58 (UFAWEE),<sup>70</sup> 59 (UFAWII)<sup>70</sup> and 60 (VAGRUC)<sup>71</sup> and the tmeda complexes 64 (IWOVAS)<sup>72</sup> and 65 (NABQEO).<sup>73</sup>

#### 4.2. "Helicite/twisted"

The category of "helicite/twisted" structures comprises binuclear complexes where the second Pd–(N)<sub>2</sub>(X)<sub>2</sub> plane is twisted in a circular fashion about the Pd⋯Pd axis through angle  $\theta_4$  (Fig. 1f and g and Table S2†). In this category, some complexes are formed from two units of a bidentate ligand ("helicite", Fig. 7a) while others contain a single unit of a tetradentate ligand ("twisted" complexes, Fig. 7b).

**4.2.1. "Helicite".** The first examples of binuclear *cis*-protected Pd(II) helicates were recently reported from our laboratory,<sup>23</sup> namely the tmeda complexes 85 (IZOJUE) and 86 (IZOKAL). The cationic units of the (P) and (M) configurations in 85 are arranged in enantiomeric stacks (Fig. 8a) *via*  $\pi$ ⋯ $\pi$  interactions.

However, in the structurally related complex 86 (IZOKAL), which contains a biphenyl spacer in the ligand backbone, the cationic units of the (P) and (M) configurations are stacked alternately through C–H⋯ $\pi$  interactions between ligand units

of adjacent cations. Further, 111 (IZOKEP) containing a terphenyl spacer in the ligand exhibits a "zigzag step" structure. The *cis*-protecting agent in these structures is tmeda, which does not contain a  $\pi$ -surface. In the bimetallic helicates 67 (ETASEY),<sup>74</sup> 68 (ETASIC)<sup>74</sup> and 69 (ETASOI)<sup>74</sup> which contain metalloligands (ML, where M is Pt), the cations assemble as chains through  $\pi$ ⋯ $\pi$  stacking interactions between the bpy units (Fig. 9).

The corresponding packing diagrams for these structures are available in the ESI† (Fig. S63–S65).

**4.2.2. "Twisted" complexes.** In the case of "twisted" complexes a uniform mode of self-assembly was not observed, but rather the molecular organisation in the solid state depends upon the ligand, *cis*-protecting units and anions. Complexes 72 (IBUHAQ)<sup>75</sup> and 73 (UJAGIV)<sup>76</sup> represent "twisted" molecules of the [Pd<sub>2</sub>(L')<sub>2</sub>(L<sup>B</sup>)(L<sup>M</sup>)<sub>2</sub>] variety, containing two pyridyl monodentate ligands and a single bidentate ligand. The cations in 72<sup>75</sup> self-assemble through C–H⋯ $\pi$  interactions between the *tert*-butyl substituted bpy groups present in the *cis*-protecting units, whereas those in 73<sup>76</sup> associate *via*  $\pi$ ⋯ $\pi$  interactions between the aromatic rings of the dimethyl bpy units. The cations in the tmeda complex, 87 (XUPKEZ),<sup>77</sup> (also of the [Pd<sub>2</sub>(L')<sub>2</sub>(L<sup>B</sup>)(L<sup>M</sup>)<sub>2</sub>] variety) assemble through C–H⋯Br interactions between the protons of en and the Br atoms of the ligand in addition to Br⋯Br interactions between ligand molecules. All other examples belonging to the "twisted" complex category consist of a tetradentate ligand coordinated to *cis*-protected Pd(II) centres. Complex 70 (OLIXOW)<sup>78</sup> formed from a metalloligand (ML, M = Li) and

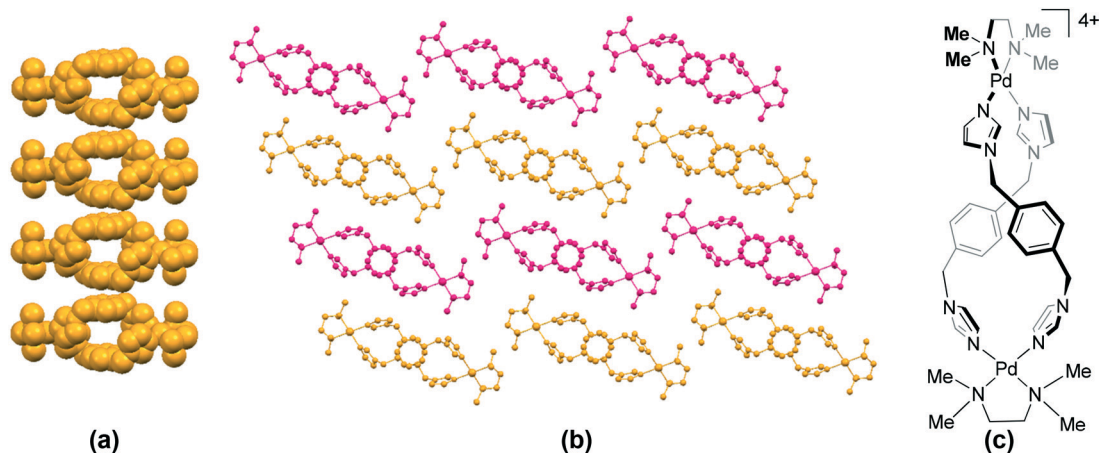


Fig. 8 Association of cations in the helicate 85 (IZOJUE)<sup>23</sup> where: (a) cations of (M) and (P) (not shown) configuration are linked by  $\pi$ ⋯ $\pi$  stacking interactions between ligand moieties; (b) top view of the molecules shows alternating rows of (P) (pink) and (M) (yellow) isomers and (c) the chemical structure of the cationic unit in 85. Some anions, solvent and hydrogen atoms and interactions are omitted for clarity.

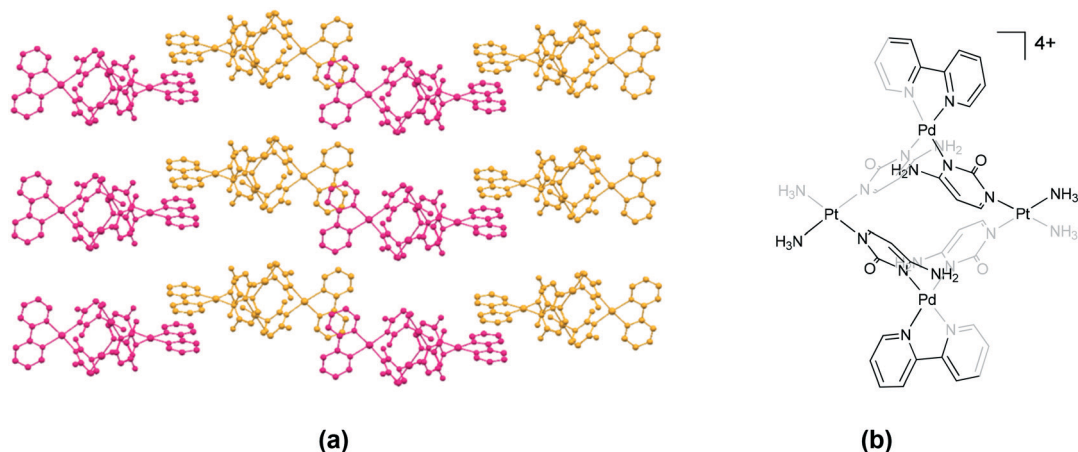


Fig. 9 Association of cations in (a) **67** (ETASEY)<sup>74</sup> through  $\pi\cdots\pi$  stacking interactions between (P) (pink) and (M) (yellow) isomers and (b) the chemical structure of the cationic unit in **67**. Some anions, solvent and hydrogen atoms and interactions are omitted for clarity.

dimethyl bpy as the *cis*-protected Pd(II) unit, contains  $\text{BPh}_4^-$  as the anion. The cations assemble through a combination of weak  $\pi$  stacking between the aromatic rings of the dimethyl bpy units and the aromatic rings of the anions. The cations in the bisacetylacetonato complexes **71** (VENCEX)<sup>79</sup> (Fig. 10) and **74** (KERBUF)<sup>80</sup> assemble through  $\pi\cdots\pi$  stacking interactions between the aromatic rings of their bpy and phen units, respectively.

The en complexes formed with the reducing sugars  $\beta$ -D-arabinopyranose,  $\beta$ -D-galactofuranose,  $\beta$ -*rac*-mannopyranose and  $\beta$ -D-ribose as the ligands, **75** (EHUOXA),<sup>81</sup> **76** (EHUDUG),<sup>81</sup> **77** (EHUFAO)<sup>81</sup> and **78** (EHUFES),<sup>81</sup> respectively, and the complexes **79** (IFOTAY),<sup>82</sup> **80** (KAKDAD),<sup>83</sup> **81** (KAKDIL)<sup>83</sup> and **82** (PIGMUO)<sup>84</sup> featuring lyxose, glucose and xylitol based ligands are also members of the “twisted” complexes category. The cations in these complexes (except for **77**) self-assemble through N–H $\cdots$ O interactions between the amine protons of en and ligand oxygen atoms to form dimers or catemers that are further linked by water molecules. In the case of **77** (EHUFAO), the molecular self-assembly is brought about by O–H $\cdots$ O hydrogen bonding interactions between the coordinated ligand molecules. In the en complexes **83**

(WIJRUD)<sup>85</sup> and **84** (WIJSK),<sup>85</sup> the cations self-assemble via C–H $\cdots$  $\pi$  interactions between the protons of en and the aromatic rings in the ligand, in addition to weak C–H $\cdots$  $\pi$  and  $\pi\cdots\pi$  interactions between the ligands of adjacent cations. The corresponding packing diagrams for these structures are available in the ESI† (Fig. S66–S81).

#### 4.3. “Plateau” and “Step”

We reported a series of binuclear complexes formed from bis(4-pyridylmethyl) piperazine and *cis*-protected Pd(II) units,<sup>86</sup> of which the bpy complex (**92**, HITHID, Fig. 11a) is of the “plateau” variety (Fig. 1a), whereas the phen (**114**, HITHOJ, Fig. 12a) and tmeda (**133**, HITHUP) complexes can be classified in the “step” category (Fig. 1b). Similarities in the molecular packing of complexes belonging to the “plateau” and “step” varieties (Tables S3 and S4†) arise due to the flattened structure of the cationic units. The “plateau” category also includes examples of the “zigzag plateau” variety (Fig. 1e).

The bpy complex **113** (HUXXAA)<sup>87</sup> also belongs to the “step” category. The cations in **92**,<sup>86</sup> **114**<sup>86</sup> and **113**<sup>87</sup> assemble primarily through  $\pi\cdots\pi$  stacking interactions

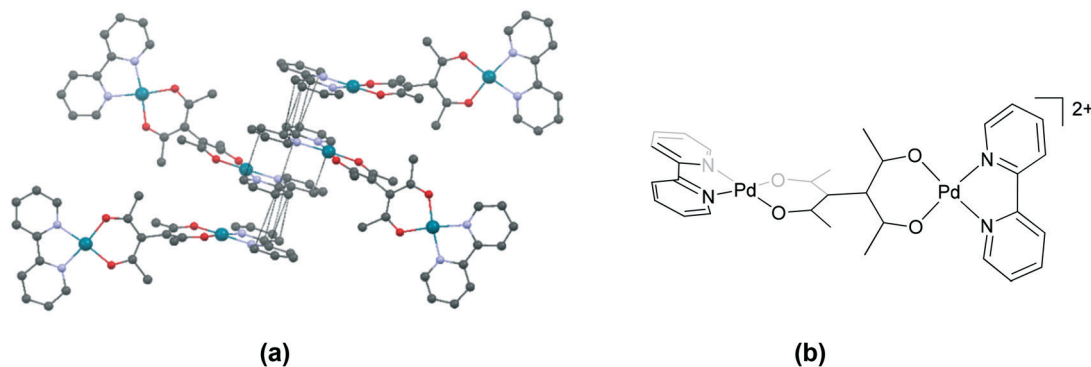
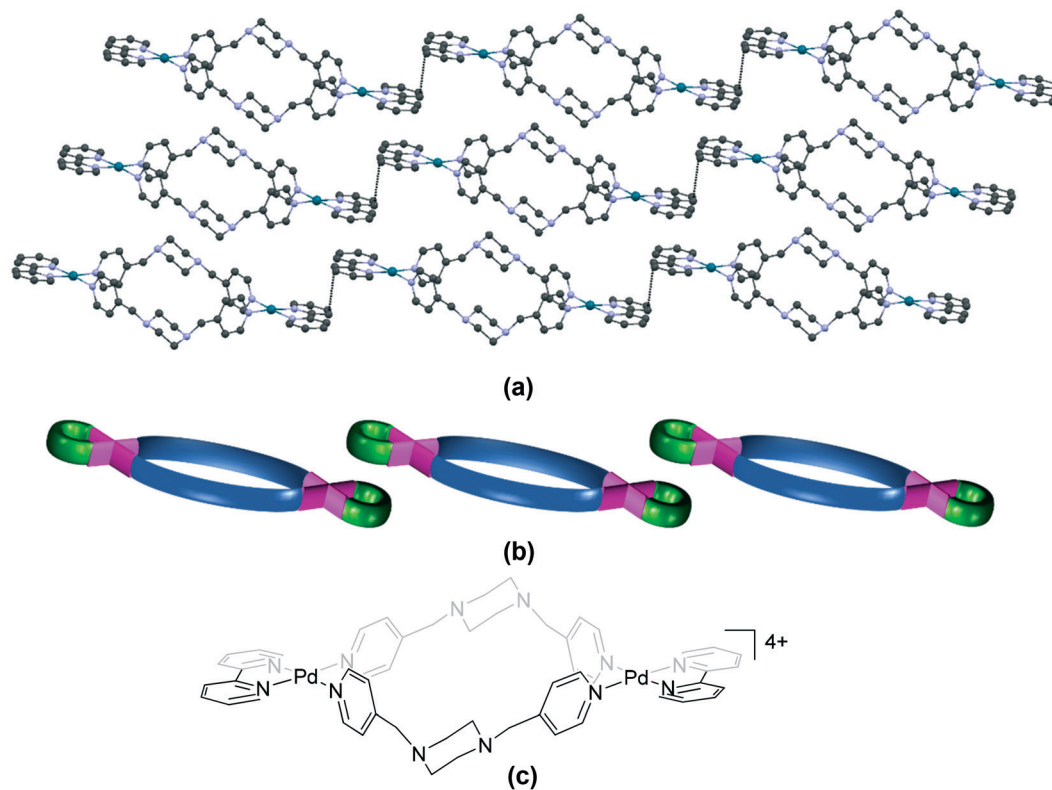


Fig. 10 Association of cations as tetrads in (a) **71** (VENCEX)<sup>79</sup> through  $\pi\cdots\pi$  interactions between the aromatic rings of bpy and (b) the chemical structure of the cationic unit in **71**. Some anions, solvent and hydrogen atoms and interactions are omitted for clarity.



**Fig. 11** Association of cations in (a) **92** (HITHID)<sup>86</sup> (“plateau”); (b) its schematic representation and (c) the chemical structure of the cationic unit in **92**. Some anions, solvent and hydrogen atoms and interactions are omitted for clarity.

between the aromatic rings of the bpy/phen units of adjacent molecules, forming a one-dimensional  $\pi$ -polymer. This mode of molecular arrangement also resembles toppled dominoes.

Some bpy and phen complexes exhibit short intramolecular Pd $\cdots$ Pd distances by virtue of the ligand's structure. The cations in these complexes self-assemble through intermolecular  $\pi\cdots\pi$  stacking interactions to form dimers which form the toppled dominoes through aromatic stacking interactions with adjacent dimers. The bpy complexes **90** (DEGKUW)<sup>88</sup> and **91** (GEJJI),<sup>89</sup> and the phen complexes **95** (JEGMUE),<sup>90</sup> **96** (WEYJUH),<sup>91</sup> **97** (WEYJUH01)<sup>92</sup> and **98** (WIVNIZ)<sup>93</sup> exhibit this type of packing in their structures. In the bpy complex **88** (AQIXON),<sup>94</sup> the cations associate in a dimeric fashion *via* aromatic stacking interactions but these dimers do not assemble as toppled dominoes due to the presence of the counteranions. There are many parallels between the modes of packing observed in the “opened jaws” complexes (section 4.1) and “plateau/step” complexes containing bpy and phen as the Pd(II) *cis*-protecting units.

The bimetallic bpy complex **89** (DAQSAQ),<sup>95</sup> and structurally related **93** (KIYKIN)<sup>96</sup> and **94** (KIYKOT)<sup>96</sup> all contain *tert*-butyl substituted bpy units. The cations assemble in a toppled domino fashion in these complexes, though no aromatic stacking interactions are observed between the bpy units. In **94**, C–H $\cdots\pi$  interactions are observed between the protons of the *tert*-butyl unit and aromatic rings of the *cis*-protecting units. The bulky *tert*-butyl units

prevent the overlap of the aromatic rings of adjacent bpy units.

The unusual bimetallic en complex **99** (DAHBOF)<sup>97</sup> of the “zigzag plateau” variety shows arrangement of the cations in the form of toppled dominoes through C–H $\cdots\pi$  interactions. Similarly, the en complexes of the [Pd<sub>2</sub>L'<sub>2</sub>(L<sup>Q</sup>)] variety, **103** (PIGMIC),<sup>98</sup> **104** (PIGNOJ)<sup>98</sup> and **105** (PIGMOI)<sup>98</sup> all contain sugar alcohols as tetraanionic polyol ligands and exhibit assembly of the cations in the form of molecular dominoes through N–H $\cdots$ O interactions between the en units and the oxygen atoms of the ligands. The related complex **106** (PIGNAV)<sup>98</sup> shows catemeric association of the cations through similar N–H $\cdots$ O interactions. The structures of the en complexes **125** (WAFTEC)<sup>99</sup> and **130** (YIQFOT)<sup>100</sup> revealed association of the cations through C–H $\cdots\pi$  and N–H $\cdots$ O interactions, respectively, giving rise to a layered arrangement. The tmeda complexes **131** (GAVDUE)<sup>101</sup> and **137** (IWOVEW)<sup>72</sup> contain aromatic rings in the ligand moiety which engage in  $\pi\cdots\pi$  stacking interactions and contribute towards the layer-like assembly of the cations.

Many of the other en (**100** (DOMBIR),<sup>102</sup> **102** (HOVWIZ),<sup>103</sup> **107** (RAKCOX),<sup>104</sup> **127** (XIVGEP),<sup>105</sup> **108** (XUQZUF),<sup>106</sup> **109** (YIMDEE)<sup>107</sup> and **110** (YIMDII)<sup>107</sup>) and tmeda (**112**, (QEGXIJ)<sup>108</sup>) complexes belonging to the “plateau” category exhibit layer-like assemblies. There are no interactions between the cationic units in these structures and hence anions, solvents and guest molecules often link the cations through hydrogen bonding contacts. Notably, the en complex

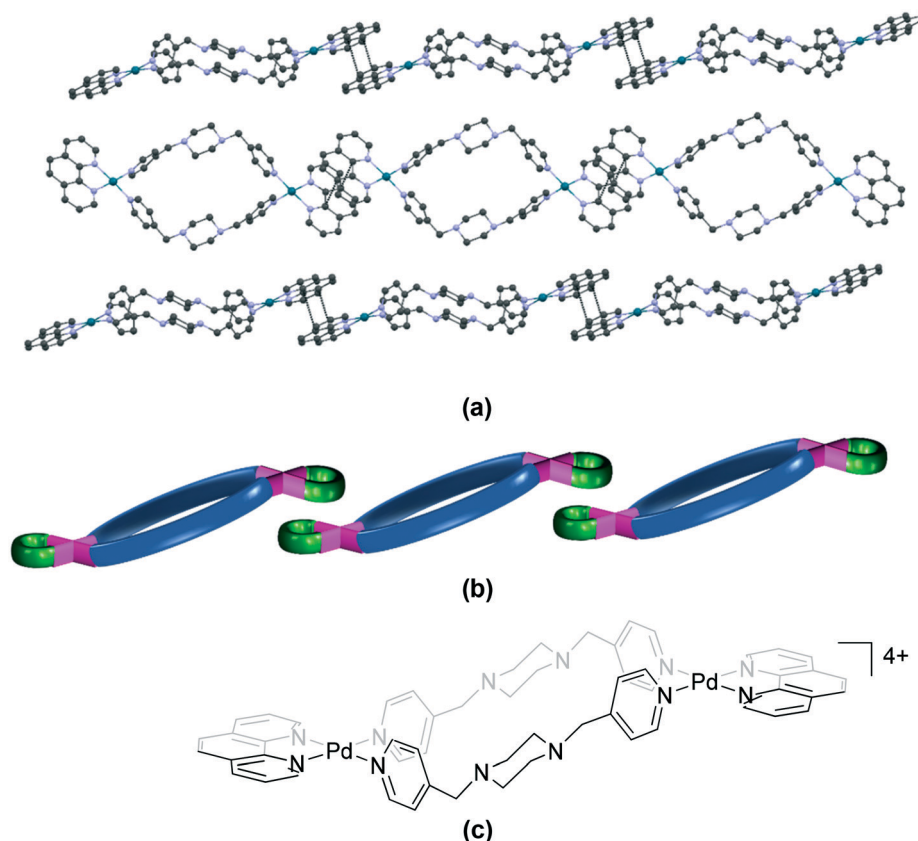


Fig. 12 Association of cations in (a) **114** (HITHOJ)<sup>86</sup> (“step”); (b) its schematic representation and (c) the chemical structure of the cationic unit in **114**. Some anions, solvent and hydrogen atoms and interactions are omitted for clarity.

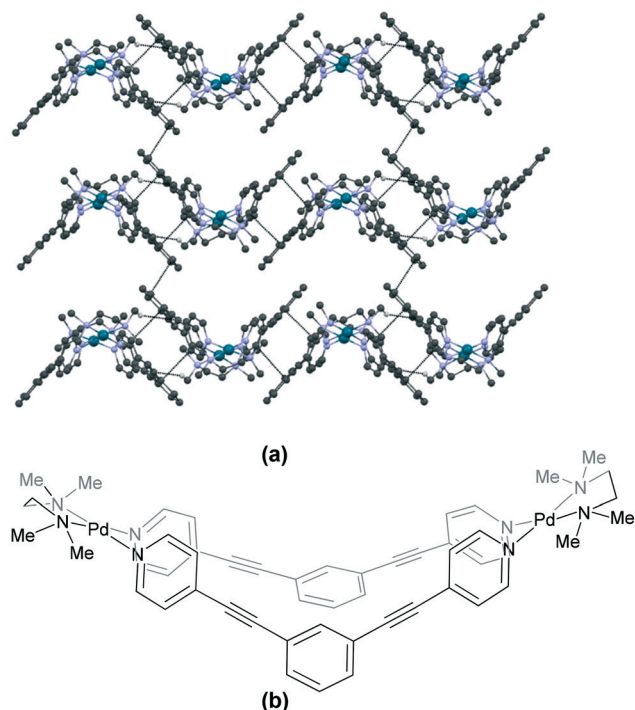
**108** (XUQZUF)<sup>106</sup> contains cations of two different conformations, namely, the “plateau” and “bow-shaped” units (discussed in the next section) in the same crystal. Unlike the related complexes **85** (IZOJUE)<sup>23</sup> and **86** (IZOKAL),<sup>23</sup> which belong to the “helicite” category, the tmeda complex **111** (IZOKEP)<sup>23</sup> is of the “zigzag step” variety. Cations assemble *via*  $\pi \cdots \pi$  stacking interactions between the phenyl rings of the ligand to form columns which are further connected by molecules of the solvent and anions.

The en and tmeda complexes of the “step” category routinely show molecular packing in the form of layers due to the flat shape of the molecule. These include the en complexes **116** (DOMBEN),<sup>102</sup> **118** (ENBAPD),<sup>109</sup> **119** (MAXHOI),<sup>110</sup> **120** (NIHVOP),<sup>111</sup> **123** (VITVEA),<sup>112</sup> **126** (XAGWOT),<sup>113</sup> **129** (XURBAO)<sup>106</sup> and the tmeda complexes **132** (GAWHUJ),<sup>114</sup> **134** (IXUQAU),<sup>115</sup> **135** (IXUQEY),<sup>115</sup> **136** (IXUQIC),<sup>115</sup> **138** (IWOVIA),<sup>72</sup> **139** (SUWVEM)<sup>116</sup> and **140** (SUWVOW).<sup>116</sup> Some of the structures exhibit zigzag or antiparallel arrangements of the layers in different directions. These include the en complex of the “plateau” variety **101** (HETQAY)<sup>117</sup> and the en complexes of the “step” variety, **115** (COCBED),<sup>118</sup> **117** (DUDPAU),<sup>119</sup> **121** (RAKCUD),<sup>104</sup> **122** (SUWVIQ),<sup>116</sup> **124** (VITVIE)<sup>112</sup> and **128** (XIVGIT).<sup>105</sup> The tmeda complexes of the “step” variety, **133** (HITHUP),<sup>86</sup> **137** (IWOVEW)<sup>72</sup> and **141** (XAYGOU),<sup>120</sup> also show zigzag arrangement of the cationic layers in their structures. These layers are interlinked with

the help of anions, solvents or included guest molecules. The corresponding packing diagrams for structures belonging to the “plateau” and “step” categories are available in the ESI† (Fig. S82–S133).

#### 4.4. “Bow-shaped”

The last category of binuclear Pd(II) complexes consists of the “bow-shaped” variety (Fig. 1c and Table S5†). A representative example is the tmeda complex **147** (WINQIV),<sup>121</sup> wherein the bow is formed by the coordination of the ligand 1,3-bis(4-pyridylethynyl)benzene to *cis*-protected Pd(II) units. The aromatic rings of the ligands of adjacent molecules are involved in  $\pi \cdots \pi$  stacking interactions leading to a molecular arrangement that appears like waves (Fig. 13). The  $\mu$ -hydroxo Pd(neocuproine) complex **142** (JIWVAO)<sup>42</sup> of the  $[\text{Pd}_2(\text{L}')_2(\text{L}^{\text{B}})]$  variety also belongs to this category. The cations assemble through  $\pi \cdots \pi$  stacking interactions between the aromatic rings of the phen units, forming wavy layers which are interconnected by the anions. The en complex **143** (DAHBUJ)<sup>97</sup> contains a metalloligand wherein a Pt atom is present at the centre of the bow. Though the cations do not directly interact with each other, the pattern of assembly resembles that observed in **142**.<sup>42</sup> The cations in the en complex **145** (ODALIO)<sup>122</sup> (which contains a glucopyranose tetrol ligand) self-assemble in a catemeric fashion through N–H $\cdots$ O interactions between the –NH protons of en and the oxygen atoms



**Fig. 13** Association of cations in (a) **147** (WINQIV)<sup>121</sup> through  $\pi \cdots \pi$  stacking interactions between the aromatic rings of the ligands of adjacent molecules, an arrangement that appears like waves and (b) the chemical structure of the cationic unit in **147**. Some hydrogen atoms and interactions are omitted for clarity.

of the ligand. The *cis*-protected Pd(II) units in the en complex **144** (XIMZID)<sup>40</sup> are held together by a bridging amidate ligand and a hydroxo bridge, giving rise to the “bow” shape.

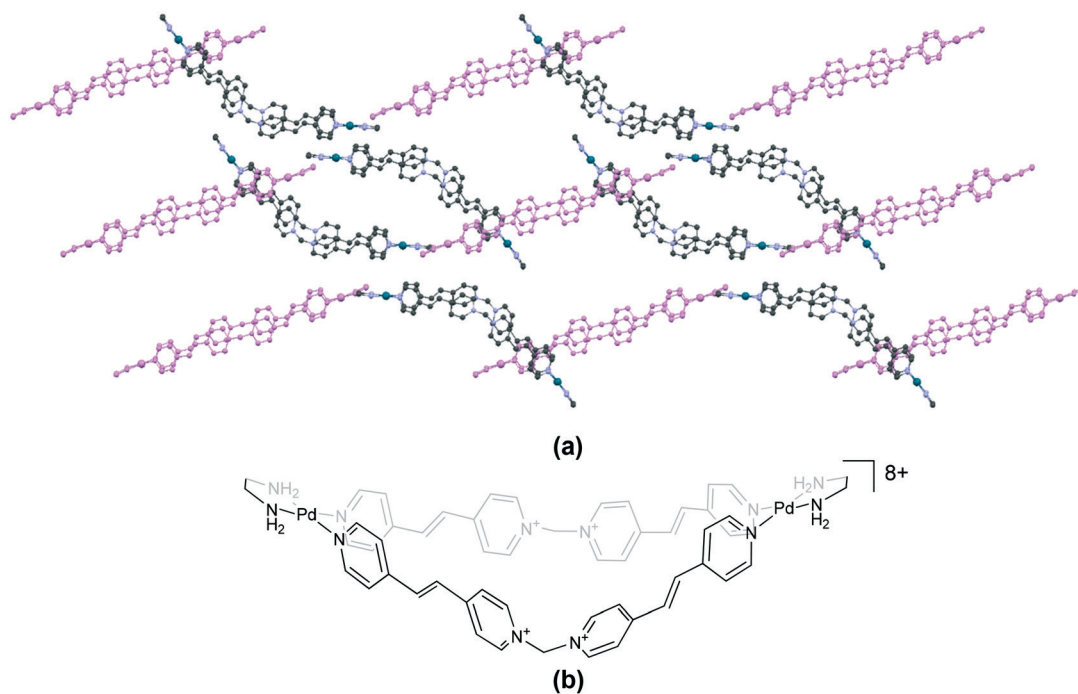
The cations of each wavy layer are linked by C–H $\cdots$ O and N–H $\cdots$ O interactions between the en unit and hydroxo oxygen atoms and the adjacent layers are interlinked by N–H $\cdots$ N interactions between the en units and amidate nitrogen atoms.

The phenyl rings of the ligand moiety play a greater role than the *cis*-protecting unit in the molecular packing of the tmeda complexes **147** (WINQIV)<sup>121</sup> and **146** (GAVDOY).<sup>123</sup> Cationic units in **146** are linked through weak C–H $\cdots$  $\pi$  interactions between the aromatic protons and phenyl rings of ligands of neighbouring molecules. The corresponding packing diagrams for these structures are available in the ESI† (Fig. S134–S138).

Finally, complex **108** (XUQZUF)<sup>106</sup> has a unique structure that contains two types of cationic units, namely, “plateau” and “bow-shaped” (Fig. 14). This phenomenon is similar to the ‘conformational isomerism’ observed in organic compounds.

## 5. Summary

In summary, five main categories of binuclear complexes could be identified based on the relative spatial orientation of the Pd–(N)<sub>2</sub>(X)<sub>2</sub> planes. The “opened jaws” structure is the most commonly observed orientation followed by the closely related “step” and “plateau” structures. The combination of the same ligand with different *cis*-protected Pd(II) units can result in structures which belong to diverse categories. Complexes containing bpy and phen moieties often tend to self-assemble through  $\pi \cdots \pi$  stacking interactions between the aromatic rings, irrespective of the type of structure. In a few cases, anions or included solvent molecules can interrupt this self-assembly by their interactions with the *cis*-protected



**Fig. 14** Assembly of two types of cations (“plateau” (violet) and “bow-shaped”) in (a) **108** (XUQZUF)<sup>106</sup> and (b) the chemical structure of the cationic unit in **108**. Some anions, solvent and hydrogen atoms and interactions are omitted for clarity.

Pd(II) units. The presence of methyl or *tert*-butyl groups on the bpy and phen aromatic rings can prevent the close approach of cationic units and hence, assembly through  $\pi$  stacking interactions. The “step” and “plateau” complexes often self-assemble as layers which are interconnected by interactions with anions and solvent molecules which occupy the gaps between adjacent layers. Some modes of self-assembly of the cationic units in the “opened jaws” and “plateau/step” architectures are comparable, particularly in the case of the *cis*-protecting units, bpy and phen. Hence, the cations can be termed ‘tectons’ which tend to self-assemble in a predictable manner through  $\pi$  stacking interactions between the aromatic rings of the *cis*-protected Pd(II) units, bpy or phen, which function as the ‘supramolecular synthons’ in these crystals. The relatively small number of crystal structures and wide variety of ligands and anions available for analysis preclude any discussion of the direct impact of the ligands’ structure or specific anions on the orientation of the Pd–(N)<sub>2</sub>(X)<sub>2</sub> planes. Many of the examples studied are complexes obtained by the combination of the ligand with a single kind of *cis*-protected Pd(II) unit; the structures of its complexes containing the other *cis*-protecting units are unknown and hence unavailable for analysis.

## 6. Outlook

The variation in the crystal structure and packing of organic molecules upon perturbation of the functional groups in the chemical structure has been well explored. Such analyses in the case of coordination complexes or metal–organic compounds have not been attempted, with the exception of coordination polymers or MOFs. The difficulties associated with conducting such a study are obtaining X-ray quality, stable crystals of large complexes, greater probability of disorder in the cationic and anionic units, inclusion of solvent or free ligand molecules in the crystal and structure solution of compounds containing many non-hydrogen atoms. The present study of structures of binuclear Pd(II) complexes reported in the CSD attempts to analyse the distinct modes of molecular packing observed upon varying the *cis*-protecting unit (bpy, phen, en, tmeda). This information is vital for the crystal engineering of pre-designed supramolecular architectures for specific functions such as anion encapsulation, guest recognition, photoluminescence and solid-state reactivity.

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## References

1 A. R. West, *Solid State Chemistry and its Applications*, John Wiley & Sons, Chichester, 1992.

- 2 (a) G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, 1989; (b) G. R. Desiraju, *Angew. Chem., Int. Ed.*, 2007, **46**, 8342; (c) G. R. Desiraju, *J. Am. Chem. Soc.*, 2013, **135**, 9952.
- 3 P. Metrangolo and G. Resnati, in *Encyclopedia of Supramolecular Chemistry*, ed. J. L. Atwood and J. W. Steed, Marcel Dekker Inc., 2004, p. 1484.
- 4 (a) H. W. Roesky and M. Andruh, *Coord. Chem. Rev.*, 2003, **236**, 91; (b) A. Nedelcu, Z. Zak, A. M. Madalan, J. Pinkas and M. Andruh, *Polyhedron*, 2003, **22**, 789; (c) K. Biradha, M. Sarkar and L. Rajput, *Chem. Commun.*, 2006, 4169; (d) J. H. Jia, P. Hubberstey, N. R. Champness and M. Schroder, in *Molecular Networks*, ed. M. W. Hosseini, 2009, vol. 132, p. 135.
- 5 (a) D. Braga, L. Brammer and N. R. Champness, *CrystEngComm*, 2005, **7**, 1; (b) A. Nangia, *Cryst. Growth Des.*, 2008, **8**, 1079; (c) C. B. Aakeroy, N. R. Champness and C. Janiak, *CrystEngComm*, 2010, **12**, 22.
- 6 (a) G. R. Desiraju, *Crystal Design: Structure and Functions (Perspectives in Supramolecular Chemistry)*, John Wiley & Sons, England, 2003; (b) *Organic Crystal Engineering: Frontiers in Crystal Engineering*, ed. E. R. T. Tiekink, J. J. Vittal and M. J. Zaworotko, John Wiley & Sons, Ltd., 2010.
- 7 G. R. Desiraju, J. J. Vittal and A. Ramanan, *Crystal Engineering: A Textbook*, World Scientific Pub. Co. Inc., Singapore, 2011.
- 8 (a) D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375; (b) J. Y. Lu, *Coord. Chem. Rev.*, 2003, **246**, 327; (c) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117; (d) D. Braga, *Acc. Chem. Res.*, 2000, **33**, 601; (e) S. R. Batten, *Curr. Opin. Solid State Mater. Sci.*, 2001, **5**, 107; (f) L. Brammer, *Chem. Soc. Rev.*, 2004, **33**, 476; (g) L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247; (h) R. Robson, *Dalton Trans.*, 2008, 5113; (i) S. R. Batten, S. M. Neville and D. R. Turner, *Coordination Polymers: Design, Analysis and Application*, Royal Society of Chemistry, Cambridge, 2008.
- 9 B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546.
- 10 (a) O. R. Evans and W. B. Lin, *Acc. Chem. Res.*, 2002, **35**, 511; (b) C. Wang, T. Zhang and W. Lin, *Chem. Rev.*, 2012, **112**, 1084; (c) C. Wang, D. Liu and W. Lin, *J. Am. Chem. Soc.*, 2013, **135**, 13222; (d) H. Reinsch, M. A. van der Veen, B. Gil, B. Marszalek, T. Verbiest, D. de Vos and N. Stock, *Chem. Mater.*, 2013, **25**, 17; (e) D.-S. Liu, Y. Sui, W.-T. Chen and P. Feng, *Cryst. Growth Des.*, 2015, **15**, 4020.
- 11 (a) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O’Keefe and O. M. Yaghi, *Science*, 2002, **295**, 469; (b) N. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O’Keefe and O. M. Yaghi, *Science*, 2003, **300**, 1127; (c) J. R. Li, R. J. Kuppler and H. C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477; (d) J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown and J. Liu, *Chem. Soc. Rev.*, 2012, **41**, 2308; (e) H. Furukawa, K. E. Cordova, M. O’Keefe and O. M. Yaghi, *Science*, 2013, **341**, 1230444.

- 12 (a) B. Kesanli and W. Lin, *Coord. Chem. Rev.*, 2003, **246**, 305 and references cited therein; (b) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450.
- 13 (a) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105; (b) Y. Yu, J.-P. Ma, C.-W. Zhao, J. Yang, X.-M. Zhang, Q.-K. Liu and Y.-B. Dong, *Inorg. Chem.*, 2015, **54**, 11590; (c) X. Li, L. Yang, L. Zhao, X.-L. Wang, K.-Z. Shao and Z.-M. Su, *Cryst. Growth Des.*, 2016, **16**, 4374; (d) H. Zhang, J. Yang, Y.-Y. Liu, S. Song and J.-F. Ma, *Cryst. Growth Des.*, 2016, **16**, 3244; (e) S. L. Jackson, A. Rananaware, C. Rix, S. V. Bhosale and K. Latham, *Cryst. Growth Des.*, 2016, **16**, 3067; (f) B. Wang, X.-L. Lv, D. Feng, L.-H. Xie, J. Zhang, M. Li, Y. Xie, J.-R. Li and H.-C. Zhou, *J. Am. Chem. Soc.*, 2016, **138**, 6204.
- 14 (a) J. J. Vittal, *Coord. Chem. Rev.*, 2007, **251**, 1781; (b) I. G. Georgiev and L. R. MacGillivray, *Chem. Soc. Rev.*, 2007, **36**, 1239; (c) L. R. Macgillivray, G. S. Papaefstathiou, T. Friscic, T. D. Hamilton, D. K. Bucar, Q. Chu, D. B. Varshney and I. G. Georgiev, *Acc. Chem. Res.*, 2008, **41**, 280; (d) W. Yuan, T. Frišćić, D. Apperley and S. L. James, *Angew. Chem., Int. Ed.*, 2010, **49**, 3916; (e) G. K. Kole and J. J. Vittal, *Chem. Soc. Rev.*, 2013, **42**, 1755.
- 15 (a) N. C. Gianneschi, M. S. Masar III and C. A. Mirkin, *Acc. Chem. Res.*, 2005, **38**, 825; (b) N. B. Debata, D. Tripathy and D. K. Chand, *Coord. Chem. Rev.*, 2012, **256**, 1831; (c) A. Schmidt, A. Casini and F. E. Kühn, *Coord. Chem. Rev.*, 2014, **275**, 19; (d) M. Han, D. M. Engelhard and G. H. Clever, *Chem. Soc. Rev.*, 2014, **43**, 1848; (e) L. Chen, Q. Chen, M. Wu, F. Jiang and M. Hong, *Acc. Chem. Res.*, 2015, **48**, 201; (f) T. R. Cook and P. J. Stang, *Chem. Rev.*, 2015, **115**, 7001.
- 16 (a) J. S. Field, L. P. Ledwaba, O. Q. Munro and D. R. McMillin, *CrystEngComm*, 2008, **10**, 740; (b) D. L. Reger, A. Debreczeni, B. Reinecke, V. Rassolov, M. D. Smith and R. F. Semeniuc, *Inorg. Chem.*, 2009, **48**, 8911; (c) D. L. Reger, A. Debreczeni and M. D. Smith, *Inorg. Chem.*, 2011, **50**, 11754; (d) X. Zhang, Z. Chi, Y. Zhang, S. Liu and J. Xu, *J. Mater. Chem. C*, 2013, **1**, 3376; (e) C. Jobbágy, M. Molnár, P. Baranyai, A. Hamza, G. Pálinkás and A. Deák, *CrystEngComm*, 2014, **16**, 3192; (f) N. Kitani, N. Kuwamura, T. Tsukuda, N. Yoshinari and T. Konno, *Chem. Commun.*, 2014, **50**, 13529; (g) T. Seki, T. Ozaki, T. Okura, K. Asakura, A. Sakon, H. Uekusa and H. Ito, *Chem. Sci.*, 2015, **6**, 2187.
- 17 (a) D. Braga, F. Grepioni, P. Sabatino and G. R. Desiraju, *Organometallics*, 1994, **13**, 3532; (b) G. R. Desiraju, *J. Mol. Struct.*, 1996, **374**, 191; (c) K. Biradha, D. Braga, F. Grepioni and G. R. Desiraju, *Organometallics*, 1996, **15**, 1284; (d) D. Braga, F. Grepioni and G. R. Desiraju, *J. Organomet. Chem.*, 1997, **548**, 33; (e) D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375; (f) D. Braga and F. Grepioni, *Coord. Chem. Rev.*, 1999, **183**, 19; (g) D. Braga, L. Maini, M. Polito, L. Scaccianoce, G. Cojazzi and F. Grepioni, *Coord. Chem. Rev.*, 2001, **216–217**, 225; (h) R. Bertani, P. Sgarbossa, A. Venzo, F. Lelj, M. Amati, G. Resnati, T. Pilati, P. Metrangolo and G. Terraneo, *Coord. Chem. Rev.*, 2010, **254**, 677.
- 18 (a) B. Moulton and M. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (b) M. Schröder and N. R. Champness, in *Encyclopedia of Supramolecular Chemistry*, ed. J. L. Atwood and J. W. Steed, Marcel Dekker Inc., 2004, p. 1420.
- 19 C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.*, 2016, **72**, 171.
- 20 (a) M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417; (b) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; (c) B. J. Holliday and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 2022; (d) M. Fujita, M. Tominaga, A. Hori and B. Therrien, *Acc. Chem. Res.*, 2005, **38**, 369; (e) B. H. Northrop, Y.-R. Zheng, K.-W. Chi and P. J. Stang, *Acc. Chem. Res.*, 2009, **42**, 1554; (f) R. Chakrabarty, P. S. Mukherjee and P. J. Stang, *Chem. Rev.*, 2011, **111**, 6810.
- 21 M. C. Naranthatta, D. Das, D. Tripathy, H. S. Sahoo, V. Ramkumar and D. K. Chand, *Cryst. Growth Des.*, 2012, **12**, 6012.
- 22 D. Tripathy, V. Ramkumar and D. K. Chand, *Cryst. Growth Des.*, 2013, **13**, 3763.
- 23 M. C. Naranthatta, S. Bandi, R. Jagan and D. K. Chand, *Cryst. Growth Des.*, 2016, **16**, 6722.
- 24 A. Hori, H. Kataoka, A. Akasaka, T. Okano and M. Fujita, *J. Polym. Sci., Part A: Polym. Chem.*, 2003, **41**, 3478.
- 25 (a) G. Ma, Y. S. Yung, D. S. Chung and J. I. Hong, *Tetrahedron Lett.*, 1999, **40**, 531; (b) D. K. Chand, K. Biradha, M. Kawano, S. Sakamoto, K. Yamaguchi and M. Fujita, *Chem. – Asian J.*, 2006, **1**, 82; (c) P. Diaz, J. A. Tovilla, P. Ballester, J. Benet-Buchholz and R. Vilar, *Dalton Trans.*, 2007, 3516.
- 26 (a) M. Fujita, O. Sasaki, T. Mitsuhashi, T. Fujita, J. Yazaki, K. Yamaguchi and K. Ogura, *Chem. Commun.*, 1996, 1535; (b) S. B. Lee, S. Hwang, D. S. Chung, H. Yun and J.-I. Hong, *Tetrahedron Lett.*, 1998, **39**, 873; (c) K. Uehara, K. Kasai and N. Mizuno, *Inorg. Chem.*, 2007, **46**, 2563.
- 27 (a) Z. Qin, M. C. Jennings and R. J. Puddephatt, *Chem. Commun.*, 2002, 354; (b) K. Uehara, H. Nakao, R. Kawamoto, S. Hikichi and N. Mizuno, *Inorg. Chem.*, 2006, **45**, 9448; (c) K. Uehara, K. Kasai and N. Mizuno, *Inorg. Chem.*, 2010, **49**, 2008; (d) S. Guha, F. S. Goodson, R. J. Clark and S. Saha, *CrystEngComm*, 2012, **14**, 1213; (e) Y. Dong, D. T. J. Loong, A. K. L. Yuen, R. J. Black, S. O'Malley, J. K. Clegg, L. F. Lindoy and K. A. Jolliffe, *Supramol. Chem.*, 2012, **24**, 508; (f) K. Uehara, T. Oishi, T. Hirose and N. Mizuno, *Inorg. Chem.*, 2013, **52**, 11200.
- 28 (a) O. Piovesana, C. Bellitto, A. Flamini and P. F. Zanazzi, *Inorg. Chem.*, 1979, **18**, 2258; (b) H.-K. Yip, T.-F. Lai and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, 1991, 1639; (c) B.-H. Xia, C.-M. Che and Z.-Y. Zhou, *Chem. – Eur. J.*, 2003, **9**, 3055; (d) S. Clement, S. M. Aly, D. Bellows, D. Fortin, C. Strohmann, L. Guyard, A. S. Abd-El-Aziz, M. Knorr and P. D. Harvey, *Inorg. Chem.*, 2009, **9**, 4118; (e) J. E. Bercaw, A. C. Durrell, H. B. Gray, J. C. Green, N. Hazari, J. A. Labinger and J. R. Winkler, *Inorg. Chem.*, 2010, **49**, 1801; (f) N. Marino, C. H. Fazen, J. D. Blakemore, C. D. Incarvito, N. Hazari and R. P. Doyle, *Inorg. Chem.*, 2011, **50**,

- 2507; (g) J. Luo, J. R. Khusnutdinova, N. P. Rath and L. M. Mirica, *Chem. Commun.*, 2012, **48**, 1532.
- 29 (a) T. Murahashi and H. Kurosawa, *Coord. Chem. Rev.*, 2002, **231**, 207; (b) V. K. Jain and L. Jain, *Coord. Chem. Rev.*, 2005, **249**, 3075.
- 30 (a) C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5525; (b) C. A. Hunter, *Chem. Soc. Rev.*, 1994, **23**, 101; (c) C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885.
- 31 J. A. R. Navarro, M. Angustias Romero and J. M. Salas, *J. Chem. Soc., Dalton Trans.*, 1997, 1001.
- 32 E. Gao, M. Zhu, H. Yin, L. Liu, Q. Wu and Y. Sun, *J. Inorg. Biochem.*, 2008, **102**, 1958.
- 33 B. Oskui and W. S. Sheldrick, *Eur. J. Inorg. Chem.*, 1999, 1325.
- 34 B. Oskui, M. Mintert and W. S. Sheldrick, *Inorg. Chim. Acta*, 1999, **287**, 72.
- 35 J. Gao, T. Riis-Johannesen, R. Scopelliti, X. Qian and K. Severin, *Dalton Trans.*, 2010, **39**, 7114.
- 36 S.-Y. Yu, M. Fujita and K. Yamaguchi, *J. Chem. Soc., Dalton Trans.*, 2001, 3415.
- 37 K. Ohno, T. Sugaya, M. Kato, N. Matsumoto, R. Fukano, Y. Ogino, S. Kaizaki, T. Fujihara and A. Nagasawa, *Cryst. Growth Des.*, 2014, **14**, 3675.
- 38 W. Micklitz, W. S. Sheldrick and B. Lippert, *Inorg. Chem.*, 1990, **29**, 211.
- 39 W.-Z. Shen, G. Trotscher-Kaus and B. Lippert, *Dalton Trans.*, 2009, 8203.
- 40 R. A. Adrian, S. Zhu, D. R. Powell, G. A. Broker, E. R. T. Tiekink and J. A. Walmsley, *Dalton Trans.*, 2007, 4399.
- 41 S. Chan and W.-T. Wong, *J. Organomet. Chem.*, 1995, **489**, C78.
- 42 N. R. Conley, L. A. Labios, D. M. Pearson, C. C. L. McCrory and R. M. Waymouth, *Organometallics*, 2007, **26**, 5447.
- 43 M. Abul-Haj, M. Quiros and J. M. Salas, *Polyhedron*, 2004, **23**, 2373.
- 44 D. M. Pearson, N. R. Conley and R. M. Waymouth, *Organometallics*, 2011, **30**, 1445.
- 45 C. Borriello, R. Centore and G. Roviello, *Inorg. Chem. Commun.*, 2005, **8**, 755.
- 46 M. Juribasic, M. Curic, K. Molcanov, D. Matkovic-Calogovic and D. Babic, *Dalton Trans.*, 2010, **39**, 8769.
- 47 T. Murahashi, T. Okuno, T. Nagai and H. Kurosawa, *Organometallics*, 2002, **21**, 3679.
- 48 M. Yu, L.-F. Wang, H.-P. Huang, S.-Y. Yu and Y.-Z. Li, *Chin. J. Inorg. Chem.*, 2006, **22**, 941.
- 49 Y. Yamada and K. Okamoto, *Chem. Lett.*, 1999, **28**, 315.
- 50 Y. Yamada, K. Fujisawa and K. Okamoto, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 2067.
- 51 H.-P. Huang, Q. Wu and G.-Q. Mei, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2006, **62**, m3465.
- 52 J. Tong, S.-Y. Yu and H. Li, *Chem. Commun.*, 2012, **48**, 5343.
- 53 M. A. Haj, M. Quiros and J. M. Salas, *J. Chem. Soc., Dalton Trans.*, 2002, 4740.
- 54 E. Alonso, J. Forniés, C. Fortuño, A. Martín, G. M. Rosair and A. J. Welch, *Inorg. Chem.*, 1997, **36**, 4426.
- 55 A. Klein and R. Lepski, *Z. Anorg. Allg. Chem.*, 2009, **635**, 878.
- 56 S. Iwatsuki, T. Itou, H. Ito, H. Mori, K. Uemura, Y. Yokomori, K. Ishihara and K. Matsumoto, *Dalton Trans.*, 2006, 1497.
- 57 K. Matsumoto, H. Moriyama and K. Suzuki, *Inorg. Chem.*, 1990, **29**, 2096.
- 58 B.-C. Tzeng, C.-S. Ding, T.-Y. Chang, C.-C. Hu and G.-H. Lee, *CrystEngComm*, 2012, **14**, 8228.
- 59 T. Murahashi, T. Okuno, K. Usui, K. Takase, T. Otani, S. Ogoshi and H. Kurosawa, *Dalton Trans.*, 2011, **40**, 2383.
- 60 R. W. Troff, R. Hovorka, T. Weilandt, A. Lützen, M. Cetina, M. Nieger, D. Lentz, K. Rissanen and C. A. Schalley, *Dalton Trans.*, 2012, **41**, 8410.
- 61 H.-P. Huang, S.-H. Lu, S.-Y. Yu, Y.-Z. Li, Q. Jiao and Y.-J. Pan, *Inorg. Chem. Commun.*, 2005, **8**, 656.
- 62 J. Vicente, J.-A. Abad, M. López-Sáez, P. G. Jones and D. Bautista, *Chem. – Eur. J.*, 2010, **16**, 661.
- 63 H.-P. Huang and L.-X. Liu, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2007, **63**, m1875.
- 64 B.-C. Tzeng, W.-F. Fu, C.-M. Che, H.-Y. Chao, K.-K. Cheung and S.-M. Peng, *J. Chem. Soc., Dalton Trans.*, 1999, 1017.
- 65 H.-P. Huang, Q. Wu, L.-X. Liu and Q.-F. Song, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2007, **63**, m458.
- 66 M. Fujita, S.-Y. Yu, T. Kusakawa, H. Funaki, K. Ogura and K. Yamaguchi, *Angew. Chem., Int. Ed.*, 1998, **37**, 2082.
- 67 S. Yu, *Private Communication*, 2014.
- 68 H.-P. Huang, H.-W. Ma and Y.-Z. Li, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2007, **63**, m1089.
- 69 S. J. Park, D. M. Shin, S. Sakamoto, K. Yamaguchi, Y. K. Chung, M. S. Lah and J.-I. Hong, *Chem. Commun.*, 2003, 998.
- 70 S. Ghosh, R. Chakrabarty and P. S. Mukherjee, *Dalton Trans.*, 2008, 1850.
- 71 R. Ahlrichs, M. Ballauff, K. Eichkorn, O. Hanemann, G. Kettenbach and P. Klufers, *Chem. – Eur. J.*, 1998, **4**, 835.
- 72 L.-Y. Yao, L. Qin, T.-Z. Xie, Y.-Z. Li and S.-Y. Yu, *Inorg. Chem.*, 2011, **50**, 6055.
- 73 Y. M. Na, T. H. Hoh, B. J. Ha, J. Hong and O.-S. Jung, *Bull. Korean Chem. Soc.*, 2009, **30**, 573.
- 74 A. Khutia, P. J. S. Miguel and B. Lippert, *Chem. – Eur. J.*, 2011, **17**, 4205.
- 75 J. Vicente, R. V. Shenoy, E. Martínez-Viviente and P. G. Jones, *Inorg. Chem.*, 2011, **50**, 7189.
- 76 J. Ruiz, M. Teresa Martínez, F. Florenciano, V. Rodríguez and G. López, *Inorg. Chem.*, 2003, **42**, 3650.
- 77 J. Vicente, R. V. Shenoy and E. Martínez-Viviente, *Organometallics*, 2009, **28**, 6101.
- 78 H. Shen, I. M. Steele and R. F. Jordan, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2003, **59**, m405.
- 79 G.-Q. Mei, K.-L. Huang, H.-P. Huang and Y.-Z. Li, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2006, **62**, m2368.
- 80 G.-Q. Mei, K.-L. Huang and H.-P. Huang, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2006, **62**, m2743.
- 81 P. Klufers and T. Kunte, *Chem. – Eur. J.*, 2003, **9**, 2013.
- 82 P. Klufers and T. Kunte, *Eur. J. Inorg. Chem.*, 2002, 1285.
- 83 T. Schwarz, D. Hess and P. Klufers, *Dalton Trans.*, 2010, **39**, 5544.



- 84 T. Allscher, X. Kastele, G. Kettenbach, P. Klufers and T. Kunte, *Chem. – Asian J.*, 2007, 2, 1037.
- 85 S. Ghosh and P. S. Mukherjee, *Organometallics*, 2007, 26, 3362.
- 86 D. Tripathy, V. Ramkumar and D. K. Chand, *Cryst. Growth Des.*, 2013, 13, 3763.
- 87 N. B. Debata, D. Tripathy, V. Ramkumar and D. K. Chand, *Tetrahedron Lett.*, 2010, 51, 4449.
- 88 R. A. Adrian, R. E. Benson, L. M. Daniels, E. R. T. Tiekink and J. A. Walmsley, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2006, 62, m601.
- 89 A. V. Eremin, D. D. Vaulina, M. A. Stepanova, V. G. Antonov, A. N. Belyaev and S. A. Simanova, *Russ. J. Gen. Chem.*, 2011, 81, 194.
- 90 M. Yu, Y.-Z. Li, L.-F. Wang, H.-P. Huang and S.-Y. Yu, *Chin. J. Inorg. Chem.*, 2006, 22, 963.
- 91 A. E. Lapshin and O. V. Magdysyuk, *Glass Phys. Chem.*, 2011, 37, 206.
- 92 A. E. Lapshin and O. V. Magdysyuk, *Glass Phys. Chem.*, 2009, 35, 627.
- 93 R. A. Adrian, G. A. Broker, E. R. T. Tiekink and J. A. Walmsley, *Inorg. Chim. Acta*, 2008, 361, 1261.
- 94 J. Garcia-Anton, J. Pons, X. Solans, M. Font-Bardia and J. Ros, *Inorg. Chim. Acta*, 2004, 357, 571.
- 95 A. Singh and P. R. Sharp, *Dalton Trans.*, 2005, 2080.
- 96 A. Singh, U. Anandhi, M. A. Cinellu and P. R. Sharp, *Dalton Trans.*, 2008, 2314.
- 97 P. Brandi-Blanco, P. J. S. Miguel and B. Lippert, *Dalton Trans.*, 2011, 40, 10316.
- 98 T. Allscher, X. Kastele, G. Kettenbach, P. Klufers and T. Kunte, *Chem. – Asian J.*, 2007, 2, 1037.
- 99 M. Fujita, S. Nagao, M. Iida, K. Ogata and K. Ogura, *J. Am. Chem. Soc.*, 1993, 115, 1574.
- 100 R. Krieglstein, D. K. Breitingner and G. Liehr, *Eur. J. Inorg. Chem.*, 2001, 3067.
- 101 T. Z. Xie, C. Guo, S. Y. Yu and Y. J. Pan, *Angew. Chem., Int. Ed.*, 2012, 51, 117.
- 102 D. Abella, V. Blanco, E. Pía, M. Chas, C. Platas-Iglesias, C. Peinador and J. M. Quintela, *Chem. Commun.*, 2008, 2879.
- 103 C. Peinador, V. Blanco and J. M. Quintela, *J. Am. Chem. Soc.*, 2009, 131, 920.
- 104 V. Blanco, M. D. García, C. Peinador and J. M. Quintela, *Chem. Sci.*, 2011, 2, 2407.
- 105 V. Blanco, M. Chas, D. Abella, E. Pía, C. Platas-Iglesias, C. Peinador and J. M. Quintela, *Org. Lett.*, 2008, 10, 409.
- 106 V. Blanco, A. Gutiérrez, C. Platas-Iglesias, C. Peinador and J. M. Quintela, *J. Organomet. Chem.*, 2009, 74, 6577.
- 107 M. Chas, D. Abella, V. Blanco, E. Pía, G. Blanco, A. Fernandez, C. Platas-Iglesias, C. Peinador and J. M. Quintela, *Chem. – Eur. J.*, 2007, 13, 8572.
- 108 G. Sanchez, J. L. Serrano, J. Garcia, G. Lopez, J. Perez and E. Molins, *Inorg. Chim. Acta*, 1999, 287, 37.
- 109 E. Sinn, C. M. Flynn Junior and R. B. Martin, *J. Am. Chem. Soc.*, 1978, 100, 489.
- 110 A. Schneider, E. Freisinger, B. Beck and B. Lippert, *J. Chem. Soc., Dalton Trans.*, 2000, 837.
- 111 M. Fujita, M. Aoyagi and K. Ogura, *Inorg. Chim. Acta*, 1996, 246, 53.
- 112 V. Blanco, M. Chas, D. Abella, C. Peinador and J. M. Quintela, *J. Am. Chem. Soc.*, 2007, 129, 13978.
- 113 C. Peinador, E. Pía, V. Blanco, M. D. García and J. M. Quintela, *Org. Lett.*, 2010, 12, 1380.
- 114 J. Ahn, K. H. Park, T. H. Noh and O.-S. Jung, *Inorg. Chem. Commun.*, 2011, 14, 1868.
- 115 J. Ahn, S. M. Kim, K. H. Park, T. H. Noh and O.-S. Jung, *Dalton Trans.*, 2011, 40, 8520.
- 116 R. S. Forgan, D. C. Friedman, C. L. Stern, C. J. Bruns and J. F. Stoddart, *Chem. Commun.*, 2010, 46, 5861.
- 117 R. Schneider, M. W. Hosseini, J.-M. Planeix, A. De Cian and J. Fischer, *Chem. Commun.*, 1998, 1625.
- 118 D. Tripathy, H. S. Sahoo, V. Ramkumar and D. K. Chand, *RSC Adv.*, 2014, 4, 18595.
- 119 V. Blanco, D. Abella, E. Pía, C. Platas-Iglesias, C. Peinador and J. M. Quintela, *Inorg. Chem.*, 2009, 48, 4098.
- 120 W.-Z. Shen, D. Gupta and B. Lippert, *Inorg. Chem.*, 2005, 44, 8249.
- 121 K. Uehara, T. Ohishi, T. Hirose and N. Mizuno, *Inorg. Chem.*, 2013, 52, 11200.
- 122 T.-Z. Xie, C. Guo, S.-Y. Yu and Y.-J. Pan, *Angew. Chem., Int. Ed.*, 2012, 51, 1177.
- 123 P. Klufers and T. Kunte, *Angew. Chem., Int. Ed.*, 2001, 40, 4210.