CHAPTER X

A New Non-covalent Bonding Mode in Supramolecular Chemistry: Main Group Element Lone-Pair-π(Arene) Interactions

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Abstract

The influence on supramolecular aggregation patterns exerted by a new synthon, main group element (M) lone-pair···π(arene) interactions, is surveyed based on data mining studies of main group element crystal structures. Zero-, one-, and less commonly, two- and threedimensional architectures are identified based on M(lp)···π(arene) interactions acting in isolation of other obvious intermolecular interactions, *e.g*. hydrogen bonding. Herein, an overview of the different aggregation patterns sustained by M(lp)···π(arene) interactions is given which, in the case of thallium(I), may occur in 13% of their crystal structures. General considerations of the formation propensities of M(lp)···π(arene) interactions, theoretical considerations and their role in macromolecular structures are also included.

X.1 Introduction

As "*the chemistry of molecular assemblies and of the intermolecular bond*",[1] supramolecular chemistry exploits a variety of non-covalent intermolecular forces to connect and organise chemical architectures constructed of molecules as building blocks (called "tectons").[2] The most common type of intermolecular interactions are hydrogen bonds,[3] donor-acceptor or dative-coordinate bonds,[4] secondary bonds or "soft-soft" interactions,[5] halogen bonds,[6] $\pi \cdots \pi$ stacking[7] and metal π-bonds.[8] Metal$\cdots\pi$(arene) bonds are well documented for transition metals with complexes such as bis(benzene)chromium, $Cr(C_6H_6)_2$, and benzenechromium tricarbonyl, $C_6H_6Cr(CO)_3$, now being historical landmarks. The bond between a transition metal atom and an arene ring is formed by donation of the π-electrons from the ring into the *d*-orbitals of the metal. This is not possible in the case of main group (post-transition) elements. However, compounds of the main group elements non-covalently bonded to benzene or other arenes have been discovered and structurally characterised by X-ray diffraction, challenging puzzled chemists for a rational explanation. Examples are the socalled Menschutkin (Menšutkin) complexes of antimony and bismuth[9] including $C_6H_6.SbCl_3$, $C_6Me_6.2SbX_3$ (with X = Cl, Br) and $C_6H_6.BiCl_3$ or $C_6Me_6.BiX_3$ (with X = Cl or Br). Metalaryl interactions were also discovered in the dimeric tin(II) dithiophosphate, $[Sn\{S_2P(OPh)_2\}_2]_2$,[10] and in the dimeric lead(II) dithiophosphonate,

$[Pb\{S_2P(OPr^i)(C_6H_4OMe\text{-}4)\}]_2$.[11] Tellurium$\cdots\pi$(arene) interactions were suggested in two compounds and their formation proposed as involving the lone-pairs of electrons interacting with the ring.[12] Thus, it was noted "*We tentatively suggest that the lone-pair is located between the* π*-bonded phenyl ring and the central tellurium atom. It is quite possible that similar weak* π*-interactions between tellurium atoms and aromatic groups are present in other* *organotellurium compounds and passed unnoticed so far*".[12] This prompted the first systematic search of the Cambridge Crystallographic Database (CSD),[13] where lonepair···π(arene) interactions were proposed as being important in molecular packing. This search revealed a significant number of tellurium compounds displaying such interactions in the solid-state, but not identified so in the original reports.[14] More recently, a new search was undertaken and the stereochemical influence of the tellurium lone-pair interaction with the πsystems investigated.[15] The data mining of the CSD[13] was extended to practically all posttransition metals,[16] *i.e.* gallium, indium and thallium,[17] tin,[18] lead,[19] arsenic,[20] antimony and bismuth,[21] and selenium.[22] In related bibliographic studies, organometallic metal carbonyl compounds were also found to form M–CO···π(arene) complexes, with intermolecular bonds leading to supramolecular associations and recognisable supramolecular architectures;[23] a more recent survey of DMSO-O(lp)···π(arene) interactions reinforces the importance of this type of contact in supramolecular chemistry.[24]

The lone-pair···π(arene) interaction[14] is now recognised as a valid bond type, both intramolecular and intermolecular, leading in the last case to supramolecular self-assembly.[14-24] DFT calculations with an exchange hole dipole moment (XDM) dispersion correction on some arsenic(III) species showed these interactions may be described as lone pair(As)···π but, interestingly, in some examples these were best described as being of the type donor(π)−acceptor(As).[25] Clearly, there is scope for further theoretical investigation in this area as proven highly informative in the cases of halogen[26] and chalcogen bonding.[27] This being stated, in the literature attention is mostly concentrated on anion···π(arene)[28] and cation···π(arene)[29] interactions rather than those involving main group elements, with the possible exception of alkali metal cations.[30] Attention is also directed towards oxygen (*e.g.*

water) and halogen lone-pair···π(arene) interactions.[31] In addition to the aromatic hydrocarbons (benzene, naphthalene, *etc*.), the π-system can be aromatic heterocycles (pyridine, triazene, *et*c.) and even some chelate rings[32] or pseudo-chelates.[33] Recently, inorganic rings, *e.g*. borazine, were also considered as potential candidates for lonepair···π(arene) ring interactions, and some theoretical calculations were performed on the assumption that the carbon-free heterocycles may display some aromatic character.[34]

The intention here is to highlight the relevance of main group element lone-pair···π(arene) interactions, abbreviated hereafter as M(lp)···π(arene), as a new non-covalent bonding mode in supramolecular chemistry. In so doing, the diversity the supramolecular aggregates sustained by these interactions will be revealed, most of which remained hidden until an appropriate analysis of the available information from the CSD[13] was performed. Most of the earlier literature reports only the molecular structures, but the analysis of their molecular packing often reveals supramolecular associations through M(lp)···π(arene) interactions.

X.2 Methodology

The Cambridge Structural Database (CSD)[13] was employed as the primary resource in data mining studies searching for M(lp)···π(arene) interactions. The CSD was searched using the program CONQUEST[35] in accord with the structural protocols shown in Fig. X.1(a). Thus, two key geometric restrictions were applied. Firstly, *d*, the distance between the main group element atom (M) and the centroid (Cg) of the arene ring was based on the sum of the halfthickness of a phenyl ring, taken as 1.9 Å, being the upper value for half the centroid-centroid distance in parallel arene rings,[7a] and the respective van der Waals radii of M,[36] plus

10% to enable the capture of all putative contacts.[37] The second criterion relates to the angle, α, which is defined as the angle between the normal to the plane through the arene ring (V_1) and the vector passing through Cg to M (V_2). The α angle was restricted to be less than 30º to ensure that only delocalised M···π(arene) interactions were extracted. Referring to Fig. 1(b), a delocalised interaction corresponds to the M atom sitting plumb or close to plumb over the ring centroid.[38] By contrast, a localised interaction would see the lone-pair directed towards a specific atom of the ring and a semi-localised interaction would have the lone-pair directed towards one bond of the ring. Preliminary screening was applied so that structures with disorder or unresolved errors were omitted along with those having other heavy metal atoms. Manual sorting of each individual "hit" ensued employing the programs PLATON[39] and DIAMOND.[40]

[Figure X.1 near here]

The manual inspection of each structure enabled the confirmation that the M(lp)···π(arene) interaction was operating in isolation of other intermolecular interactions. An example of this concept is illustrated in Fig. X.2. Referring to this figure, in binuclear and centrosymmetric $\{Sn[S_2P(OPh)_2]_2\}_2$,[10] one phenyl ring of each bidentate bridging dithiophosphate ligand is directed over the centrosymmetrically-related tin atom enabling a putative Sn(lp)···π(arene) interaction. Here, d = 3.66 Å and α = 19.6º, fulfilling the standard geometric restrictions mentioned above. However, along with the Sn(lp)···π(arene) interaction, secondary interactions,[5] of the type Sn···S [3.04 Å] also occur so that the Sn(lp)···π(arene) interactions are not "stand-alone", but operate in concert with the Sn···S contacts, and therefore the structure was not regarded as having independent Sn(lp)···π(arene) interactions and therefore, is not included herein. On this basis, a good number of the initial "hits" from the CSD searches were excluded often owing to the presence of the aforementioned secondary interactions and to hydrogen bonding. Finally, it should be noted that the putative Sn(lp)···π(arene) interaction in $[Sn\{S_2P(OPh)_2\}_2]_2$[10] is recognised, on geometric grounds, as a contact by the ubiquitous structure analysis program, PLATON.[39] Despite this, it is still rare for M(lp)···π(arene) interactions to be commented upon in the primary literature.

[Figure X.2 near here]

In the ensuing sections, selected examples of M(lp)···π(arene) points of contact found in indium(I),[17] thallium(I),[17] tin(II),[18] lead(II),[19] arsenic(III),[20] antimony(III),[21] bismuth(III),[21] selenium(II and IV)[22] and tellurium(II and IV)[15] crystal structures are presented, in this order. Examples were selected on the basis of novelty and aesthetics: the interested reader is referred to the original exhaustive reviews for full details for each element. Diagrams were drawn/redrawn with the aid of DIAMOND,[40] with all hydrogen atoms omitted, and the accompanying chemical structure diagram only includes the species participating in the M(lp)···π(arene) interaction, *i.e*. typically counter-ions, solvents, *etc*. are not included.

X.3 Overview of M(lp)···π(arene) interactions

X.3.1 Indium(I)

The chemistry of gallium and indium with the element in the +I oxidation state is not very well developed,[41] there being relatively few examples, certainly when compared with the farranging chemistry of thallium(I). There is in fact only one example of an indium(I) structure featuring an In(lp)···π(arene) interaction, namely $[In\{OC_6H_2(CF_3)_3\text{-}2,4,6\}]_2$, (**2**).[42] The molecule is binuclear with each of the crystallographically independent indium atoms forming an In(lp)···π(arene) interaction [*d* = 3.87 Å and α = 7.6º; 4.22 Å, 18.0º]. The supramolecular aggregation sustained by these interactions is a zigzag chain as illustrated in Fig. X.3.

[Figure X.3 near here]

X.3.2 Thallium(I)

The centrosymmetric binuclear aggregate illustrated in Fig. X.4(a) and found in the structure of [2-(2',6'-di-isopropylphenylamido)-4-(2',6'-di-isopropylphenylimino)-2-pentene] thallium(I),[43.] (**3**), and supported by a pair of Tl(lp)···π(arene) interactions [*d* = 3.92 Å and α = 11.0º] is a common motif found for thallium(I) and indeed other main group elements. Higher nuclearity, zero-dimensional aggregates are also known. For example, in the crystal structure of $Tl[N(SiMe_3)C_6H_3(iPr)_2\text{-}2,6]$,[44].(**4**), centrosymmetric tetranuclear aggregates involving both crystallographically independent molecules are formed and feature four Tl(lp)···π(arene) interactions [*d* = 3.11 Å and α = 11.7º; 3.12 Å, 9.6º], Fig. X.4(b).

[Figure X.4 near here]

One-dimensional aggregation is found for {(η^5-diphenylphosphanyl-tetramethylcyclopentadienyl)thallium(I),[45] (**5**), with each molecule accepting and donating a

Tl(lp)···π(arene) interaction [d = 3.60 Å and α = 19.6º]. The topology of the chain is zigzag, Fig. X.5.

[Figure X.5 near here]

X.3.3 Tin(II)

The centrosymmetric dimeric motif features prominently among tin(II) compounds forming Sn(lp)···π(arene) interactions.[18.] An example, [Sn{N(Ph)=C(Me)C(H)=C(Me)N(Ph)}Cl],[46] (**6**), where the pyramidal N_2Cl donor set is capped by an arene ring [d = 3.46 Å and α = 4.9º], is illustrated in Fig. X.6.

[Figure X.6 near here]

The mixed oxidation state tetranuclear compound, $[\{Sn(O_2CMe)_2\}_2O]_2$, crystallises as a mono-benzene solvate (**7**) with the benzene located about a 2-fold axis of symmetry.[47.] The exocyclic tin(II) atoms form Sn(lp)···π(arene) interactions [d = 3.32 Å and α = 6.1º] to generate a somewhat twisted supramolecular chain, Fig. X.7(a). In $(Me_3Si)_2NSn[OC_6H_2(tBu_2)$-2,6-Me-4],[48.] (**8**), with two-coordinate tin(II) atoms, a supramolecular zigzag chain is formed as shown in Fig. X.7(b) [d = 3.76 Å and α = 1.2º]. Binuclear bis(μ$_2$-N-(2-oxidophenyl)salicylideneiminato)-di-tin(II),[49] (**9**), has crystallographically imposed 2-fold symmetry and features a tetra-coordinated tin(II) centre within a NO_3 donor set. The flat portions of centrosymmetrically-related molecules face each other to facilitate the formation of Sn(lp)···π(arene) interactions [d = 3.53 Å and α = 5.6º], with the two donor and two acceptor interactions per molecule leading to a supramolecular chain with a twisted topology, Fig. X.7(c).

[Figure X.7 near here]

X.3.4 Lead(II)

As mentioned above in X.3.2, the zero-dimensional dimeric aggregate illustrated in X.4(a) is a common motif. A variation on this motif is found for Pb($SC_6H_3Me_2$-2,6)$_2$($NC_5H_4NMe_2$4),[50] (**10**), where the dimeric aggregate sustained by two Pb(lp)···π(arene) interactions [*d* = 3.52 Å and α = 12.7°] has 2-fold symmetry, Fig. X.8(a). The asymmetric unit of Pb(C_6H_4Br4)$_2$,[51] (**11**), contains two independent molecules and each is located on a crystallographic centre of inversion. A linear supramolecular chain is formed as both independent lead(II) atoms form two apparent Pb(lp)···π(arene) interactions [*d* = 3.62 Å and α = 6.5°; *d* = 3.67 Å and α = 8.0°], Fig. X.8(b). The formation of two Pb(lp)···π(arene) interactions is perhaps unexpected and the nature of these still unclear. It is possible that the lone-pair of electrons is arranged spherically around the lead(II) centre. Another view is that one of the interactions is of the type Pb(lp)···π(arene) and the other being a transition metal-like π(arene)···Pb interaction.

[Figure X.8 near here]

The two-coordinate lead(II) atom in (N,N'-di-neopentyl-1,2-phenylenediamino)lead(II),[52] (**12**), lies on a crystallographic mirror plane. Again, each lead(II) atom forms two apparent Pb(lp)···π(arene) interactions with one being significantly longer than the other [*d* = 3.18 Å and α = 6.1º; *d* = 3.97 Å and α = 10.1º]. The arene ring accepts both interactions and the result is a two-dimensional arrangement as illustrated in Fig. X.9. The topology of the layer is flat with the neopentyl groups lying to either side.

[Figure X.9 near here]

X.3.5 Arsenic(III)

One-dimensional supramolecular chains sustained by As(lp)···π(arene) interactions are often observed in the crystal structures arsenic(III) compounds.[20.] An exception is found in the centrosymmetric dimeric aggregate in the structure of $[(2,6\text{-}Me_2C_6H_3N)AsCl]_3$,[53] (**13**), Fig. X.10(a) [*d* = 3.78 Å and α = 14.2º]. A truly remarkable supramolecular association is found in the structure of chloro-(toluene-3,4-dithiolato)arsenic(III),[54] (**14**), Fig. X.10(b). Here, the supramolecular chain, with a zigzag topology is stabilised by As(lp)···π(arene) interactions [*d* = 3.30 Å and α = 3.6º]. This occurs despite their being both chloride and sulphur in the compound, each capable of forming As···Cl and/or As···S secondary interactions;[5] the closest As···Cl separation of 3.82 Å is beyond the sum of their respective van der Waals radii.[36] A supramolecular chain is also found in the structure of $(PhAsO)_4$,[55] (**15**). Here, only one of the four arsenic(III) atoms of the eight-membered ring compound forms a As(lp)···π(arene) interactions [*d* = 3.52 Å and α = 11.8º]; the chain has a linear topology, Fig. X.10(c). The three examples mentioned here have the common feature of a pyramidal coordination geometry with a capping arene ring.

[Figure X.10 near here]

X.3.6 Antimony(III)

A full range of supramolecular architectures sustained by Sb(lp)···π(arene) interactions exists.[21] Zero-dimensional aggregates are well-known and are exemplified by dimeric and centrosymmetric (*p*-tol)$SbCl_2$,[56] (**16**), Fig. X.11(a) [*d* = 3.30 Å and α = 11.5º]. In dichloro(8-(dimethylamino)naphthyl)antimony(III),[57] (**17**), a supramolecular chain with an helical topology is formed as a result of Sb(lp)···π(arene) interactions [*d* = 3.88 Å and α = 15.7º], Fig. X.11(b). A zigzag supramolecular chain is formed in the structure of Sb($SC_6H_3Me_2$3,5),[58] (**18**), mediated by Sb(lp)···π(arene) interactions [*d* = 3.29 Å and α = 8.0º], Fig. X.11(c). As with the arsenic(III) structures cited above, no secondary Sb···S contacts are formed in the crystal structure of **18**.

[Figure X.11 near here]

A flat supramolecular layer having Sb(lp)···π(arene) interactions is found in the crystal structure of [(t-BuN)Sb($C_6H_3Me_2$-2,6)]$_2$,[59] (**19**), Fig. X.12. The four-membered cyclic molecule is disposed about a 2-fold axis of symmetry. Each antimony(III) atom donates a lone-pair of electrons and each ring accepts an interaction, meaning four points of contact per molecule [*d* = 3.92 Å and α = 1.2º] contributing to the layer assembly.

[Figure X.12 near here]

X.3.7 Bismuth(III)

A wide range of zero-dimensional aggregates sustained by Bi(lp)···π(arene) interactions have been noted.[21] Centrosymmetric dimeric units are found in the structure of bis-[2(dimethylaminomethyl)phenyl]-iodido-bismuth(III), (**20**),[60] Fig. X.13(a) [*d* = 3.92 Å and α = 18.4º]. A higher nuclearity aggregate is found in (2.2.2)paracyclophane tris[trichloridobismuth(III)],[61] (**21**), in which each arene ring accepts a Bi(lp)···π(arene) interaction. As the molecule lacks symmetry, there are three independent contacts [*d* = 2.98 Å and α = 10.5º;

2.99 Å, α = 5.6º; *d* = 3.08 Å, α = 3.5º], Fig. X.13(b).

[Figure X.13 near here]

Examples of linear and helical supramolecular chains are found in the crystal structures of Ph_3Bi,[62] (**22**), and $Bi(OC_6H_3Me_2\text{-}2,6)_3$,[63] (**23**), respectively, Figs X.14(a) and (b). Each molecule of each chain participates in an acceptor and donor Bi(lp)···π(arene) interaction [**22**: *d* = 3.76 Å and α = 11.0º; **23**: *d* = 2.99 Å, α = 3.3º].

[Figure X.14 near here]

In a compound closely related to **19** (see Fig. X.12), *i.e.* $[(t\text{-}BuN)BiPh]_2$,[64] (**24**), the centrosymmetric binuclear molecules participate in four Bi(lp)···π(arene) interactions [*d* =

3.92 Å and α = 10.1º] to form a supramolecular layer with a flat topology, Fig. X.15.

[Figure X.15 near here]

X.3.8 Selenium(II, IV)

The familiar zero-dimensional dimeric aggregate is found in the structure of the [$MeSeC(=CH_2)CH_2N^+(H)Me_2$] cation,[65] (**25**), with the exception being there is no crystallographic symmetry relating the molecules so there are two independent Se(lp)···π(arene) interactions supporting the aggregate, Fig X. 16(a). The parameters describing these interactions are equivalent, *i.e*. *d* = 3.82 Å and α = 26.5º, suggesting a pseudo centrosymmetric arrangement. The selenium(II) atom may be embedded within a ring, as in 5-phenyl-selenazolidine-2,4-dione,[66] (**26**), and still form a Se(lp)···π(arene) interaction. In the case of **26**, this interaction [*d* = 3.53 Å and α = 4.6º] results in a supramolecular chain with a helical topology, Fig. X.16(b). An example of an unusual aggregate results when the selenium atoms are directly connected as in the diselenide derivative [$2\text{-}MeOC_6H_4C(=O)Se]_2$,[67] (**27**). There are two independent diselenide molecules in the crystallographic asymmetric unit. One selenium(II) atom in each molecule forms a Se(lp)···π(arene) interaction [*d* = 3.90 Å and α = 26.4º; *d* = 3.93 Å and α = 12.7º]. The shorter interactions occur between centrosymmetrically-related molecules, and the resulting dimeric aggregate accepts two Se(lp)···π(arene) interactions from a second set of symmetryrelated independent molecules with the result that a four-molecular aggregate is formed, Fig. X.16(c). Viewed in another perspective, both arene rings of one independent molecule participate in Se(lp)···π(arene) interactions while the arene rings of the second molecule participate in no such interactions.

[Figure X.16 near here]

In binuclear molecules where the selenium atoms are well separated, if each participates in a Se(lp)···π(arene) interaction, higher aggregation patterns will ensue. This is realised in the structure of [PhSe(Cl)C=C(Cl)SePh],[68] (**28**). Here, the molecule is centrosymmetric, and forms two interactions [*d* = 3.80 Å and α = 24.4º] resulting in a linear supramolecular chain, Fig. X.17(a). A variation is found in the structure 1,2,4,5-tetrafluoro-3,6bis(phenylseleno)benzene,[69] (**29**), for which two independent molecules comprise the crystallographic asymmetric unit, each of which is disposed about a centre of inversion. Only one of the molecules forms Se(lp)···π(arene) interactions [*d* = 3.99 Å and α = 27.2º] to lead to a supramolecular layer with a flat topology, Fig. X.17(b).

[Figure X.17 near here]

Selenium in the form of doubly-bonded selenide can also form Se(lp)···π(arene) interactions. An example of this is found in the structure of 2-phenyl-2,3-dihydro-1,3,2benzothiazaphosphole 2-selenide,[70] (**30**), with the interactions [*d* = 3.52 Å and α = 17.6º] leading to a zigzag supramolecular chain, Fig. X.18(a).

Se(lp)···π(arene) interactions have been found to occur between charged species as for example in the bicyclic salt $[Ph_4P]_2[As_4Se_6]$,[71] (**31**). As shown in Fig. X.18(b), two selenium(II) atoms form Se(lp)···π(arene) interactions [*d* = 3.63 Å and α = 11.6º; 3.96 Å and α = 22.6º], bridging one of the independent Ph_4P^+ anions to form a linear supramolecular chain.

[Figure X.18 near here]

Selenium(IV), with one lone-pair of electrons, rather than two found in selenium(II) compounds, can also form Se(lp)···π(arene) interactions. This is illustrated for PhSe(=O)OH,[72] (**32**), where these interactions [*d* = 3.50 Å and α = 17.2º] lead to linear supramolecular chains, Fig. X. 18(c).

The final compound to be discussed in this section is also a salt, namely $[PhN^+Me_3][SeBr_4]\{2[Se_2Br_2]\bullet 2Br^-\}$,[73] (**33**), bearing both selenium(II) and selenium(IV) centres. The selenium(IV) atom, located on a crystallographic centre of inversion, is coordinatively saturated precluding its participation in Se(lp)···π(arene) interactions. One of the selenium(II) atoms forms two independent Se(lp)···π(arene) interactions [*d* = 3.51 Å and α = 4.7º; 3.93 Å and 25.1º] with the same arene ring to form a flat supramolecular layer, Fig. X.19.

[Figure X.19 near here]

X.3.9 Tellurium(II, IV)

Despite not being isomorphous, the supramolecular aggregation sustained by Te(lp)···π(arene) interactions in the crystal structure of [PhTeC(Cl)=C(Cl)TePh],[74] (**34**), matches that of the selenium(II) analogue, *i.e.* **28**, Fig. X.17(a). The Te(lp)···π(arene) interactions [d = 3.76 Å and α = 12.4º] lead to a linear supramolecular chain as shown in Fig. X.20.

[Figure X.20 near here]

A rare example of a three-dimensional architecture sustained by M(lp)···π(arene) interactions is found in the structure of [4-ClC$_6$H$_4$TeTeC$_6$H$_4$Cl$_4$-4],[75] (**35**), Fig. X.21. The ditelluride molecule lacks symmetry but each tellurium(II) atoms forms a Te(lp)···π(arene) interaction [d = 3.67 Å and α = 9.5º; 3.81 Å and 19.6º]. The molecule has the approximate shape of the letter L with four points of contact involving Te(lp)···π(arene) interactions resulting in the stabilisation of a three-dimensional structure.

[Figure X.21 near here]

The final three structures to be described feature tellurium(IV) centres. The centrosymmetric dimeric aggregate motif is found in the crystal structure of (4-MeOC$_6$H$_4$)Te[(Ph)C=C(H)SPh]Cl$_2$,[76] (**36**), Fig. X.22(a), stabilised by Te(lp)···π(arene) interactions [d = 3.41 Å and α = 0.9º]. Another example of a supramolecular aggregate sustained by Te(lp)···π(arene) interactions is the zigzag chain in the crystal structure of [Ph(Cl)C=CH]$_2$TeCl$_2$,[77] (**37**), Fig. X.22(b); [d = 3.76 Å and α = 12.4º].

[Figure X.22 near here]

The last structure to be described poses a dilemma in the assignment of the putative Te(lp)···π(arene) interactions akin to that noted in the structures of $Pb(C_6H_4Br\text{-}4)_2$,[51] (**11**), Fig. X.8(b), and (N,N'-di-neopentyl-1,2-phenylenediamino)lead(II),[52] (**12**), Fig. X.9. The tellurium(IV) centre in bis(2,2'-biphenylylene)-tellurium(IV),[78] (**38**), forms two almost identical interactions with two arene rings as illustrated in Fig. X.22(c). The parameters associated with these interactions are d = 3.72 Å and α = 11.1°, and d = 3.72 Å and α = 11.6°. The resulting assembly is a supramolecular linear chain.

X.4 Biological relevance

While the recognition of M(lp)···π(arene) interactions in main group element systems is a relatively recent phenomenon, it is likely that the first report of such an interaction was in the macromolecular literature.[79] Referring to Fig. X.23, the cytidine-sugar oxygen atom, O4', interacts with the pyrimidine ring of a guanine residue, *i.e.* representing an O(lp)···π(pyrimidine) interaction similar to the M(lp)···π(arene) interactions described. By contrast to many of the structural papers in molecular main group element chemistry, the original authors of this work highlighted the role of the O(lp)···π(pyridimidine) interactions as being important in stabilising the Z-DNA conformation.[79] In several of the previous surveys of M(lp)···π(arene) interactions, analogous interactions operating in macromolecular systems were also noted.[17,21,22]

[Figure X.23 near here]

While a comprehensive survey of M(lp)···π(arene) interactions in macromolecular structures is not appropriate here, one structure is particularly worthy of highlighting. As shown in Fig. X.24, an interaction of a telluride atom incorporated within the five-membered ring of a guanidine residue occurs in a synthetic oligonucleotide.[80] This Te(lp)···π(arene) [d = 3.56 Å and α = 12.7º] interaction does not have a precedent in the molecular chemistry of tellurium; selenium examples are known, however; see X.3.8.

[Figure X.24 near here]

X.5 Conclusions and Outlook

The foregoing discussion indicates that M(lp)···π(arene) interactions exercise a very real role in the supramolecular chemistry of the main group elements, leading to well-defined zero-, one- and more rarely, two- and three-dimensional supramolecular assemblies.[16-22] Thallium(I) compounds are the most likely to form these types of interactions, being found in nearly 14% of thallium(I)-containing structures. This number is greater than the 9% probability for bismuth(III) to form Bi(lp)···π(arene) interactions which in turn is higher than 6% for antimony(III), selenium(II, IV) and tellurium(II, IV) compounds. The least likely elements to form M(lp)···π(arene) interactions are arsenic(III) (4%), and tin(II) and lead(II) (2 ~ 3%) compounds. As noted previously,[16-22] no correlations exist between d and α. In some bismuth(III) series of compounds, systematic variations in d were successfully correlated to differences in electronegativity of bismuth(III) centres as well as the π-systems.[21.]

A complete theoretical understanding of M(lp)···π(arene) interactions is a work in progress.

However, there appears to be some consensus that the attributes leading to halogen bonding may be relevant in this context. Thus, there is polarity in the electron distribution of the lonepair of electrons so that there is an electron deficiency at the tip of the lone-pair of electrons and a build-up of electron density around the girth. The electron-rich π-system thereby interacts with the electropositive region at the tip of the lone-pair.[81,82] However, as noted in the Introduction, dispersion-corrected DFT calculations reveal that these interactions may be sometimes described as donor(π)−acceptor(As) interactions,[25] consistent with aforementioned "additional" contacts mentioned for (**11**)[51], (**12**)[52] and (**38**)[78]. The latter observations indicate more theoretical work is required to fully appreciate the nature of these interactions.

Clearly, M(lp)···π(arene) interactions may participate in the stabilisation of crystal structures and their presence should be identified during any crystal structure analysis. Future work will be devoted to fully understanding the chemical nature of the bonding behind these interactions, investigation of the relative importance of semi-localised and localised M(lp)···π(arene) interactions, and expanding the range of aromatic systems that can participate in M(lp)···π(arene) interactions, perhaps being inspired by macromolecular structures.

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X.5 References

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Figure Captions

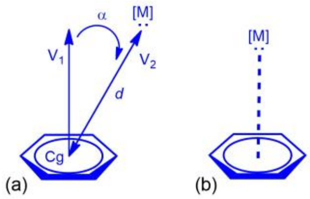

Fig. X.1 (a) Search protocols for the identification of M(lp)···π(arene) interactions in structure included in the Cambridge Structural Database: *d* is the distance between the main group element (M) and the centroid (Cg) of the arene ring, and the angle, α, is defined as the angle between the normal to the plane through the arene ring (V_1) and the vector passing through Cg to M (V_2), and (b) A representation of a delocalised M(lp)···π(arene) interaction whereby the main group element (M) sits plumb to the plane of the arene ring or deviates from the vertical by no more than 30º.

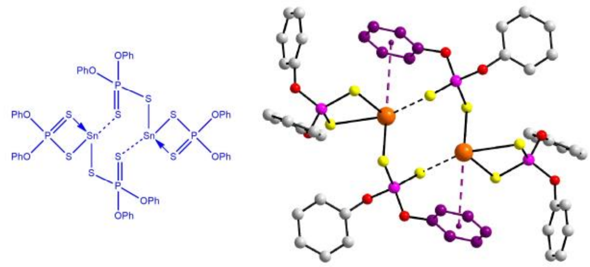

Figure X.2 Chemical diagram and molecular structure of supramolecular dimer $[Sn\{S_2P(OPh)_2\}_2]_2$, (**1**), being an example of a structure excluded from consideration as having an independent Sn(lp)···π(arene) interaction because the dimer is also sustained by Sn···S secondary bonding (black dashed lines). Colour code: orange, main group element; yellow, sulphur; pink, phosphorous; red, oxygen; grey, carbon; purple, carbon of the interacting arene ring; purple dashed line, the M(lp)···π(arene) interaction.

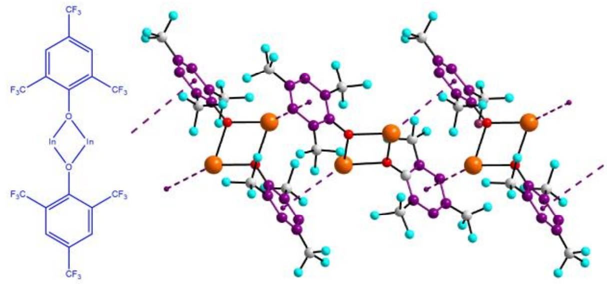

Figure X.3 Chemical diagram of $[In\{OC_6H_2(CF_3)_3\text{-}2,4,6\}]_2$, (**2**), and the supramolecular chain sustained by In(lp)···π(arene) interactions. Additional colour code: aqua, fluoride or other halide.

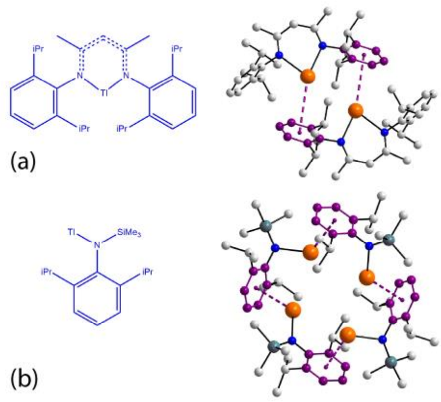

Figure X.4 Chemical diagrams of (a) [2-(2',6'-di-isopropylphenylamido)-4-(2',6'-diisopropylphenylimino)-2-pentene]thallium(I), (**3**), and (b) $Tl[N(SiMe_3)C_6H_3(iPr)_2\text{-}2,6]$, (**4**), and supramolecular aggregates sustained by Tl(lp)···π(arene) interactions. Additional colour code: hunter green, silicon; blue, nitrogen.

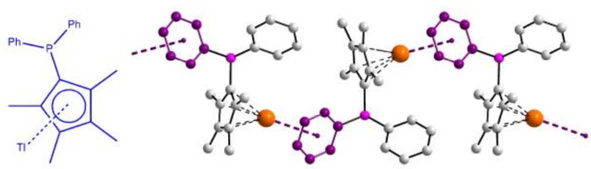

Figure X.5 Chemical diagram of {(η^5-diphenylphosphanyl-tetramethyl-cyclopentadienyl)thallium(I), (**5**), and the supramolecular chain sustained by Tl(lp)···π(arene) interactions.

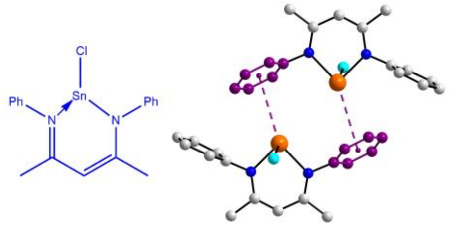

Figure X.6 Chemical diagram of [Sn{N(Ph)=C(Me)C(H)=C(Me)N(Ph)}Cl], (**6**), and the supramolecular dimer sustained by Sn(lp)···π(arene) interactions.

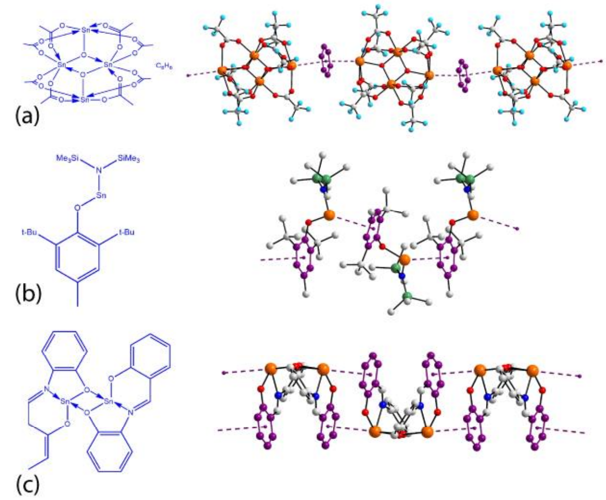

Figure X.7 Chemical diagrams of (a) $[\{Sn(O_2CMe)_2\}_2O]_2.C_6H_6$, (**7**), (b) $(Me_3Si)_2NSn[OC_6H_2(tBu_2)$-2,6-Me-4], (**8**), and (c) bis(μ_2-N-(2-oxidophenyl)salicylideneiminato)-di-tin(II), (**9**), and supramolecular chains sustained by Sn(lp)···π(arene) interactions.

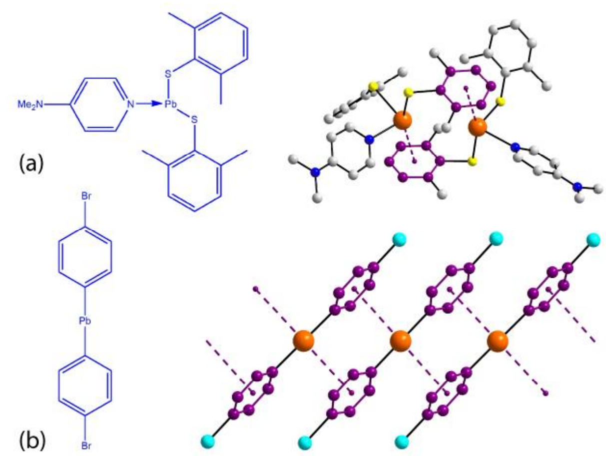

Figure X.8 Chemical diagrams of (a) $Pb(SC_6H_3Me_2\text{-}2,6)_2(NC_5H_4NMe_2\text{-}4)$, (**10**), and (b) $Pb(C_6H_4Br\text{-}4)_2$, (**11**), and supramolecular aggregates sustained by Pb(lp)···π(arene) interactions.

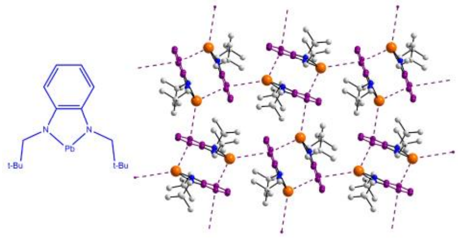

Figure X.9 Chemical diagram of (N,N'-di-neopentyl-1,2-phenylenediamino)lead(II), (**12**), and the supramolecular layer sustained by Pb(lp)···π(arene) interactions.

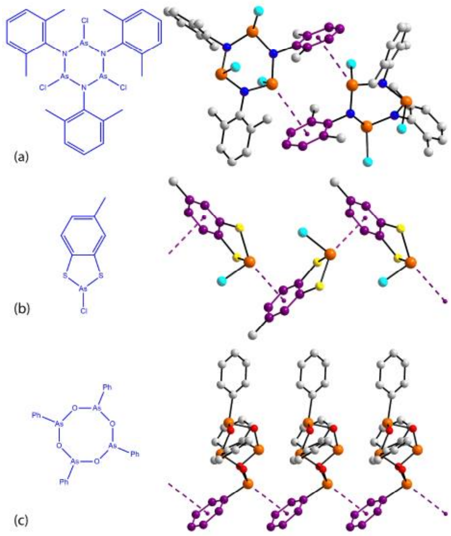

Figure X.10 Chemical diagrams of (a) $[(2,6\text{-}Me_2C_6H_3N)AsCl]_3$, (**13**), (b) chloro-(toluene3,4-dithiolato)arsenic(III), (**14**), and (c) $(PhAsO)_4$, (**15**), and supramolecular aggregates sustained by As(lp)···π(arene) interactions.

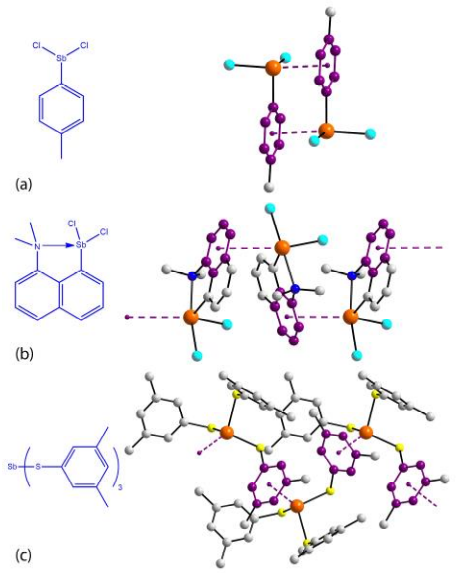

Figure X.11. Chemical diagrams of (a) (p-tol)$SbCl_2$, (**16**), (b) dichloro-(8(dimethylamino)naphthyl)antimony(III), (**17**), and (c) $Sb(SC_6H_3Me_2\text{-}3,5)_3$, (**18**), and supramolecular aggregates sustained by Sb(lp)···π(arene) interactions

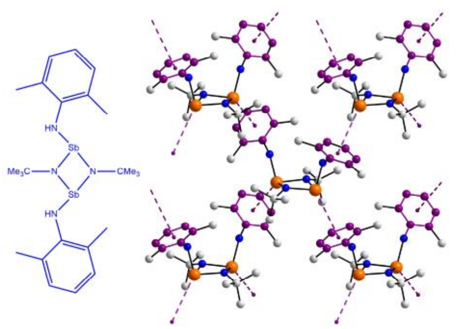

Figure X.12 Chemical diagram of $[(t\text{-}BuN)Sb(C_6H_3Me_2\text{-}2,6)]_2$, (**19**), and the supramolecular layer sustained by Sb(lp)···π(arene) interactions.

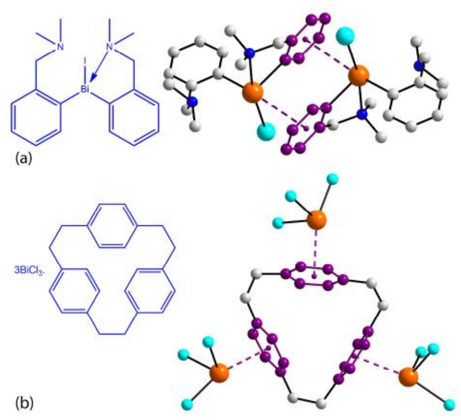

Figure X.13 Chemical diagrams of (a) bis-[2-(dimethylaminomethyl)phenyl]-iodido-bismuth(III), (**20**), and (b) (2.2.2)paracyclophane tris[trichlorido-bismuth(III)], (**21**), and their supramolecular aggregates sustained by Bi(lp)···π(arene) interactions.

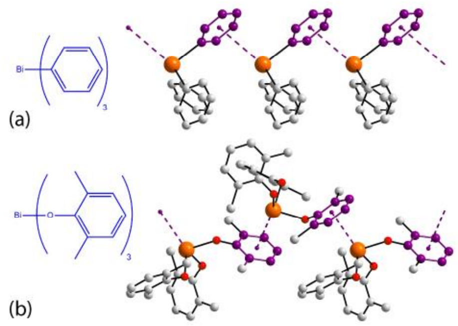

Figure X.14 Chemical diagrams of (a) Ph_3Bi, (**22**), and (b) $Bi(OC_6H_3Me_2\text{-}2,6)_3$, (**23**), and their supramolecular chains sustained by Bi(lp)···π(arene) interactions.

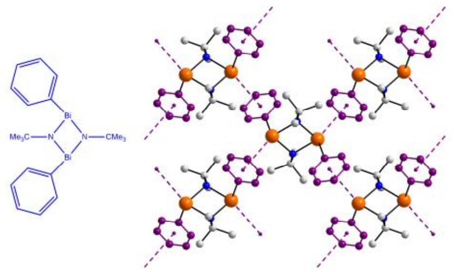

Figure X.15 Chemical diagram of $[(t\text{-}BuN)BiPh]_2$, (**24**), and the supramolecular layer sustained by Bi(lp)···π(arene) interactions.

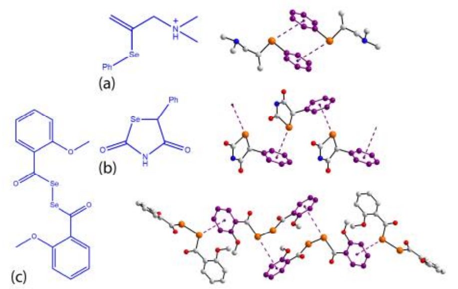

Figure X.16 Chemical diagrams of (a) $[MeSeC(=CH_2)CH_2N^+(H)Me_2]$, (**25**), (b) 5-phenylselenazolidine-2,4-dione, (**26**), and (c) $[2\text{-}MeOC_6H_4C(=O)Se]_2$, (**27**), and their supramolecular aggregates sustained by Se(lp)···π(arene) interactions.

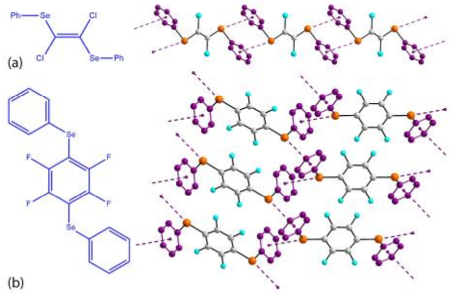

Figure X.17 Chemical diagrams of (a) [PhSe(Cl)C=C(Cl)SePh], (**28**), and (b) 1,2,4,5tetrafluoro-3,6-bis(phenylseleno)benzene, (**29**), and their supramolecular aggregates sustained by Se(lp)···π(arene) interactions.

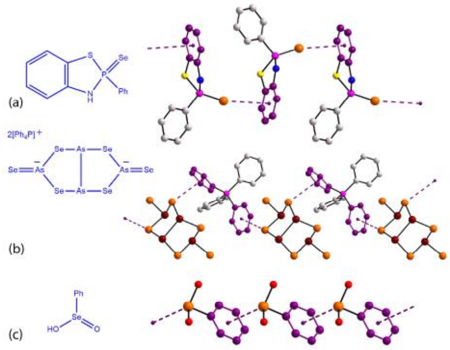

Figure X.18. Chemical diagrams of (a) 2-phenyl-2,3-dihydro-1,3,2-benzothiazaphosphole 2selenide, (**30**), $[Ph_4P]_2[As_4Se_6]$ (**31**), and (c) PhSe(=O)OH, (**32**), and their supramolecular chains sustained by Se(lp)···π(arene) interactions.

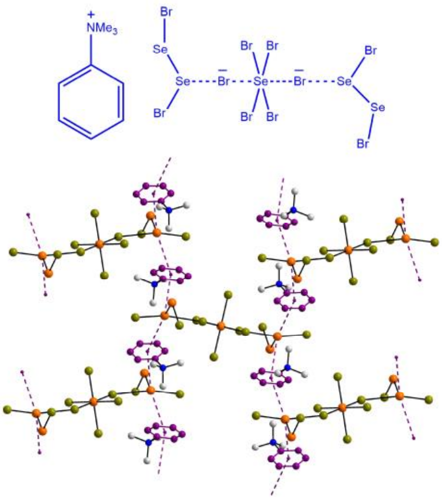

Figure X.19 Chemical diagram of $[PhN^{+}Me_3][SeBr_4]\{2[Se_2Br_2].2Br^{-}\}$, (**33**), and the supramolecular layer sustained by Se(lp)···π(arene) interactions.

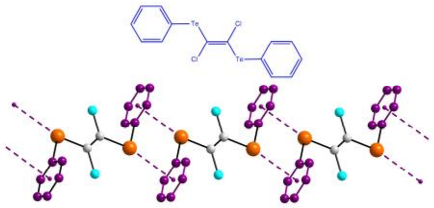

Figure X.20 Chemical diagram of [PhTe(Cl)C=C(Cl)TePh], (**34**), and the supramolecular chain sustained by Te(lp)···π(arene) interactions.

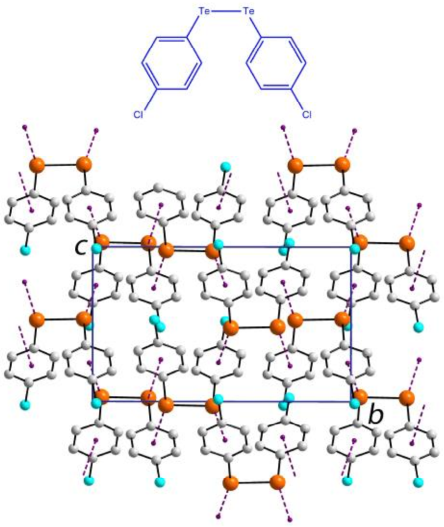

Figure X.21 Chemical diagram of [4-ClC_6H_4TeTe$C_6H_4Cl_4$-4], (**35**), and a view of the threedimensional supramolecular architecture sustained by Te(lp)···π(arene) interactions.

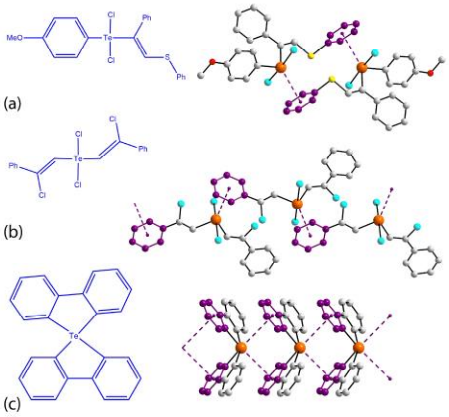

Figure X.22 Chemical diagrams of (a) (4-MeOC_6H_4)Te[(Ph)C=C(H)SPh]Cl_2, (**36**), (b) [Ph(Cl)C=CH]$_2$TeCl_2, (**37**), and (c) bis(2,2'-biphenylylene)-tellurium(IV), (**38**), and their supramolecular aggregates sustained by Te(lp)···π(arene) interactions.

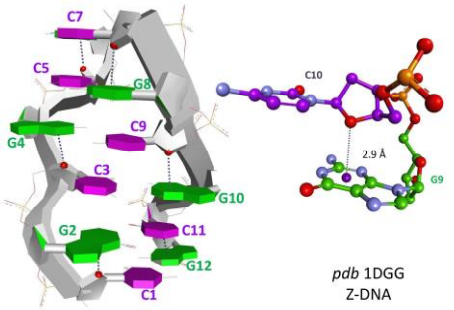

Figure X.23 Images highlighting the O(lp)···π(ring) interaction between the cytidine-sugarO(lp) and the pyrimidine ring of a guanine residue in left-handed Z-DNA.

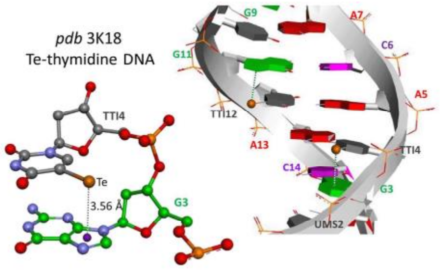

Figure X.24 Images highlighting the Te(lp)···π(ring) interaction of a doubly-bonded telluride atom interacting with the five-membered ring of a guanidine ring.