Main group supramolecular chemistry†‡

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Metal directed self-assembly has yielded a wide array of two- and three-dimensional structures with fascinating new chemical properties. These structures have typically been prepared utilizing transition metals as directing units, owing to the well-defined coordination preferences these metals exhibit. An area of growing research interest involves the preparation of structures containing main group elements as directing units. This *tutorial review* surveys the wide range of structure types available through this approach, specifically covering unique structure types accessible from the unusual coordination geometries often exhibited by the elements in Groups 12–17 of the periodic table. This review should be of interest to supramolecular and main group chemists, and researchers in the fields of crystal engineering, host–guest chemistry, and molecular recognition.

1. Introduction

The field of supramolecular chemistry has produced numerous examples of chemically interesting and aesthetically pleasing self-assembled structures using metals as directing elements.[1–3] The self-assembly process that guides the formation of these thermodynamically stable architectures is thought to have many advantages over traditional stepwise syntheses in accessing large and ordered structures.[1] Most of these assemblies leverage the predictable and well-characterized coordination preferences of the transition metals—typically octahedral, square planar or tetrahedral. A growing area of interest, however, lies in the exploration of main group metals as directing elements in order to access structure types previously unattainable through traditional means.[4] The main group elements possess unique coordination preferences and electronic properties observed rarely in the rest of the periodic table, presenting unique opportunities for the preparation of novel structures with new and interesting characteristics.[5–7] This *tutorial review* highlights examples of self-assembled supramolecular structures comprising main group elements with a focus on the unusual coordination geometries often observed in these assemblies.

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† The HTML version of this article has been enhanced with colour images.

‡ We would like to dedicate this tutorial review to Prof. Kenneth N. Raymond on the occasion of his 65th birthday.

Scope of review

The main group elements are typically defined as the set of s and p block elements, plus zinc, cadmium, and mercury.[5] For the purposes of this review, we mainly consider the heavier p block elements, and we focus on supramolecular structures containing main group complexes bearing unusual coordination geometries. Some notable examples of main group supramolecular complexes found in tetrahedral or octahedral coordination environments are also included. To limit the scope of this review, we highlight key representative examples of the complexes found from Groups 12–17. Complexes in Group 12 are particularly challenging to separate into "main group" *versus* transition metal-type complexes, as zinc tends to behave more as a transition metal in terms of reactivity and coordination and often appears in general supramolecular reviews. Mercury, however, tends to display the unusual coordination geometries common to the main group elements and will be discussed in section 3. Finally, structures containing Group 1 and 2 elements are not covered, and the reader is referred to recent reviews.[8]

The *types* of structures reviewed include discrete, polynuclear complexes *without* bonds between the main group ions. We also exclude organometallic main group complexes and those in which the multiple main group elements are bridged by simple halogen or chalcogen ions to form dimers or larger complexes. This review focuses on discrete self-assembled metal–ligand complexes where the main group ion is a directing element for the self-assembly reaction. Throughout the review, we are careful to note where the properties and coordination geometries of the main group elements depart from those expressed by the transition metals. Given the unusual coordination preferences of the main group ions, we first classify these coordination spheres, followed by a more detailed discussion of the individual supramolecular structures.

2. Coordination geometries of main group elements

The set of coordination geometries most commonly observed with transition metal complexes is relatively small and limited compared with the main group metals. Ligand distributions far removed from the typical tetrahedral and octahedral arrangements are frequently observed in complexes containing elements from Groups 13–15; these unusual structures are intimately linked with the unique electronic properties of these elements.[7] The heavier main group elements such as lead(II) and thallium(I) are stabilized in unexpectedly low oxidation states due to relativistic stabilization of s orbitals. The presence of this "inert pair" of electrons often results in some of the more unusual hemidirected coordination spheres observed in main group complexes.

Tetrahedral and octahedral ligand distributions are frequently observed with the trivalent Group 13 elements, such as aluminium, gallium, and indium. A selection of the coordination geometries of particular relevance is illustrated in Fig. 1, in which *a* and *b* indicate the more common tetrahedral and octahedral coordination spheres, respectively. Less common are the trigonal bipyramid (*c*), disphenoidal (*d*), square pyramidal (*e*), and trigonal pyramidal (*f*) coordination geometries.

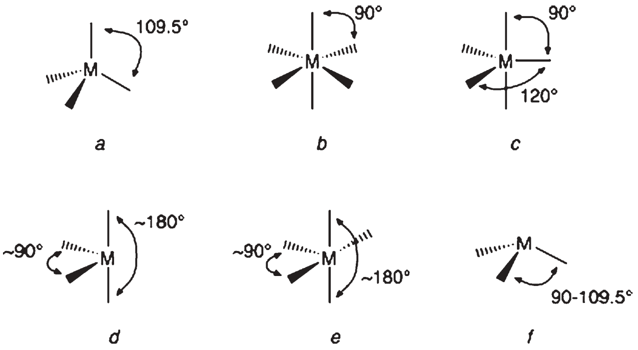

Fig. 1 Coordination geometries commonly observed in main group coordination complexes. The bond angles shown correspond to the idealized coordination geometries. Depending on the nature of the bonding in each case, the precise angles may vary. This is quite pronounced in the trigonal pyramidal geometry *f*, where increasing p character in the bonding can reduce the bond angles to near 90°.

Coordination geometries common to the heavier p-block elements often exhibit stereoactive lone pairs, but these preferences are less predictable. Particularly common are trigonal pyramidal (observed often with the pnictogens), square pyramidal, and disphenoidal (observed frequently in Pb(II) complexes) coordination geometries about the metal center.

3. Group 12—zinc, cadmium, and mercury

The Group 12 elements are a somewhat special case when considering the chemistry of the main group elements. Zinc in particular resembles a transition metal in both reactivity and coordination preferences and has been used extensively in the preparation of supramolecular structures. The literature on this topic is certainly too broad to be considered here and has been discussed in many general supramolecular reviews.[1,3,9] Cadmium displays similar properties and coordination preferences to zinc, although it does possess a preference for softer Lewis base donors, similar to its softer main group brethren. In particular, trigonal planar coordination of three cysteine thiolates is used to assemble tripeptide bundles about a Cd(II) center.[10]

Mercury(II)-containing supramolecular structures, however, tend to have much more in common with main group elements, in part because of their propensity to form structures with low-coordinate linear or other distorted coordination geometries. This fact has been used to direct the formation of a variety of macrocyclic structures, some of which exhibit novel guest binding properties. Mercury(II) is not often included in the design of well-ordered, discrete supramolecular complexes. In the few examples of supramolecular mercury complexes, the Hg(II) ion typically adopts either two-coordinate, linear geometries or a distorted tetrahedral, nearly disphenoidal-type of geometry. An example of the disphenoidal geometry occurs when mercury(II) is coordinated to adenine-*N*1-oxide in an Hg_2L_2 macrocyclic structure (Fig. 2).[11] While distorted from ideality, one can clearly observe the nearly linear (155°) arrangement of the Cl–Hg–Cl triad, as well as a much sharper angle (96.7°) between the oxygen and nitrogen donors.

An elegant example of mercury(II)-directed self-assembly combines both the lability of Hg–N bonds as well as hydrogen

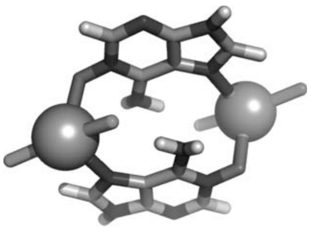

Fig. 2 $Hg_2L_2Cl_2$ macrocycle where L is adenine-*N*1 oxide. Hg(II) atoms are separated by 7.43 Å.

bonding to influence the structure.[12] The twofold symmetric dipyridyl ligands shown in Fig. 3 contain both a metal-coordination site and a pair of hydrogen bond donor/acceptors. The nature of the structure formed depends exquisitely on the presence or absence of *one* methylene group between the pyridine and the amide linkage or between the central phenylene ring and the amide linkage—without these methylene groups, an $Hg_2L_2X_2$ (X = Cl, Br, I) macrocycle forms, while with the methylene groups, polymers and sheets form. In the structure lacking the methylene linkages, two intramolecular hydrogen bonds stabilize the macrocycle. Both THF and dichloroethane (DCE) have been found in the cavity. The Hg(II) atoms in the structure are separated by 12.77 Å, while the distance between the aromatic rings of the two ligands measures approximately 7.68 Å when DCE is encapsulated. Another pyridine-containing Hg macrocycle has been prepared with a much larger ester-linked diphenyl-fluorene backbone and bridging two *meta*-substituted pyridine rings (Fig. 4).[13] The cavity formed in this macrocycle is significantly larger than the previously described macrocycle; the Hg atoms are separated by 16.68 Å and the distance between the two central, quaternary carbon centers is 15.04 Å. The crystal structure of this macrocycle reveals several disordered water molecules in the cavity.

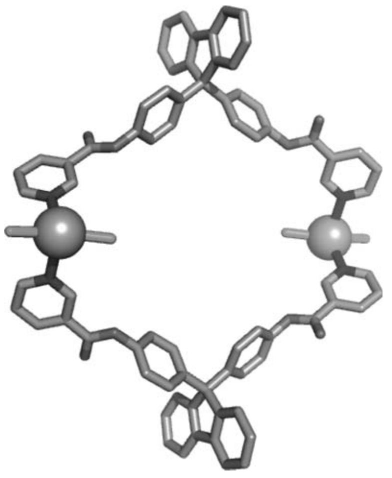

Fig. 4 Expanded dinuclear Hg(II) macrocycle. The larger fluorene based ligands provide a much larger cavity; disordered water molecules have been removed for clarity. The Hg(II) centers are separated by 16.68 Å, while the distance between the quaternary fluorene carbons is 15.04 Å.

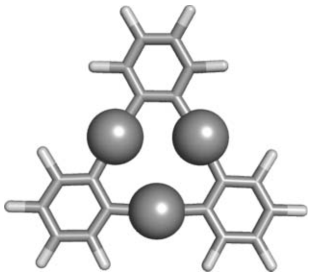

Fig. 5 A planar, trinuclear Hg(II) macrocycle bridged by *ortho*-substituted perfluorophenyl ligands; the average Hg(II)···Hg(II) distance is 3.63 Å.

The tendency of Hg(II) to form linear coordination complexes has been used to prepare a series of trinuclear macrocycles.[14] While these structures fall into the realm of organometallic chemistry by virtue of the Hg–carbon bonds that connect the components, these complexes are a striking example of main group elements as integral parts of a macromolecular assembly. In this case, the ligand is an *ortho* substituted tetrafluorophenyl ring, with Hg(II)–C bonds occupying these two *ortho* positions. The linearly-coordinated Hg(II) ions form the edges of an equilateral triangle capped by the *ortho* substituted ligands, with an average Hg–Hg distance of 3.63 Å. The Hg_3L_3 macrocycle has been successfully co-crystallized with a wide variety of organic compounds which generally do not penetrate the cavity of the macrocycle, but rather are complexed to the exterior of the macrocycles. A representative example of a Hg_3L_3 structure is shown in Fig. 5.

Icosahedral carboranes such as *closo*-1,2-$C_2B_{10}H_{12}$ (*ortho*) and *closo*-1,7-$C_2B_{10}H_{12}$ (*meta*) have also been used to great effect in the preparation of tri- and tetranuclear macrocycles of mercury(II), also referred to as mercuracarborands or

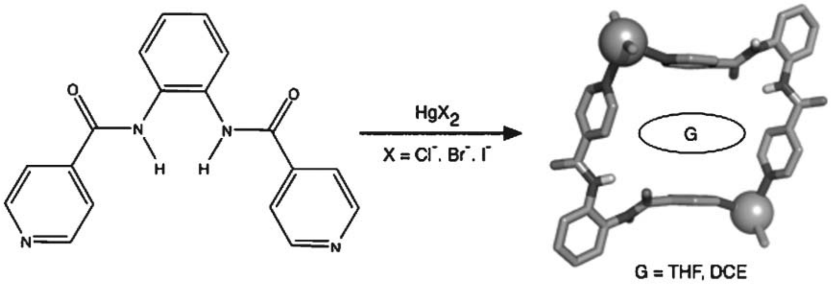

Fig. 3 Formation of an $Hg_2L_2Cl_2$ macrocycle whose structure depends strongly on the geometry of an intramolecular hydrogen bond. Hg(II) cations are separated by 12.77 Å, while the two pyridyl rings interacting with the guest are separated by 7.68 Å.

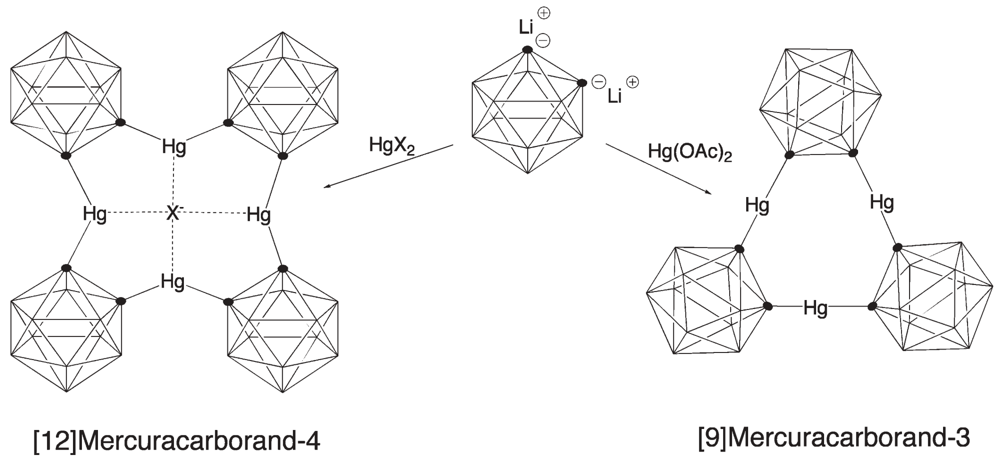

Fig. 6 Synthesis of mercuracarborands with halide template (left, [12]-mercuracarborand-4) and without halide template (right, [9]-mercuracarborand-3). Vertices of polyhedra represent boron, while solid dots represent carbon. Hydrogens are omitted for clarity.

"anti-crown" reagents (due to their anion binding properties).[15] The formation of tri- *versus* tetranuclear structures is dependent on the presence of an anion template—when halide salts of Hg(II) are employed, a planar, tetranuclear macrocycle ([12]mercuracarborand-4) is obtained. A variety of structures form based on the size of the halide template. For example, when $HgCl_2$ is the Hg(II) source, the chloride is coordinated to all four mercury atoms in a square-planar fashion *inside* the macrocycle. Bromide and iodide, however, are both too large to fit inside the macrocycle and are therefore coordinated to the Hg(II) ions out of the plane of the tetranuclear macrocycle. If Hg(II) salts such as acetate are used instead, the template effect is lost and a trinuclear macrocycle forms. (Fig. 6). These triangles exhibit a rich host–guest chemistry of their own, including the formation of sandwich-type structures with both iodide and benzene in the solid state. (See Section 8.)

Hg(II) also forms a variety of supramolecular complexes with amino acid derived ligands. Cysteine, for example, assembles with Hg(II) to form an M_4L_4 supramolecular square where each terminal thiolate group bridges two metal cations.[16]

While Hg(II) often adopts the aforementioned linear coordination sphere, a trigonal *tris*-thiolato structure can be enforced by use of a *de novo* designed peptide sequence to assemble tripeptide bundles similar to those reported with Cd(II).[10]

4. Group aluminium and gallium

The Group 13 metals have recently emerged as important building blocks in the fabrication of self-assembled supramolecular structures. Aluminium, gallium, and indium are generally found as trivalent cations and consequently have a preference for harder donor ligands based on oxygen and nitrogen and tend to take on predictable tetrahedral and octahedral coordination geometries. Multibranched chelating ligands based on β-diketonates, catecholates, hydroxamates, and other such groups have been used to great effect in the rational synthesis of supramolecular structures.

An interesting example of an Al_4L_4 square structure has been prepared from 2-hydroxybenzoxazole and trimethylaluminium, where each Al(III) loses one methyl group and is coordinated by two ligands.[17] The resulting tetrahedral aluminum center comprises each corner of the square, and it is bridged by coordination of a hydroxyl oxygen on one ligand and an oxazole nitrogen on a second ligand. (Fig. 7) Most supramolecular structures with a square topology such as this are formed from *cis*-square planar coordination to metal centers—in this case, the tetrahedral geometry around the corner units induces a bent structure analogous to cyclobutane.

A representative example of the many metallohelicates prepared from trivalent main group metals is shown in Fig. 8. The dihydroxypyridinone ligand shown on the left forms an Al_2L_3 helicate as a racemic mixture of ΔΔ and ΛΛ isomers. This molecule encapsulates one guest water molecule in the center of its cavity in the crystalline state; in solution, the complex converts slowly from the chiral enantiomers to an achiral ΔΛ *meso* structure. When this ligand is treated with Ga(III), however, the ΔΛ mesocate is observed in the crystalline state. In solution the structure rapidly interconverts between the achiral and chiral forms as a result of a fast Bailar twist at the metal centers. This rather uncommon example of the same ligand driving the formation of two different isomers is thought to be caused by the relatively small size of Al(III) compared with Ga(III). The small Al(III) center should make the trigonal prismatic intermediate in a Bailar

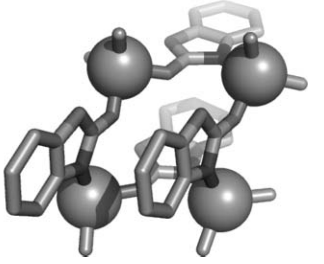

Fig. 7 Al_4L_4 molecular square with tetrahedral aluminium(III) centers bridged by 2-hydroxybenzoxazole ligands. The unusual tetrahedral coordination mode observed in the tetranuclear square complex induces a distorted shape akin to that observed in cyclobutane.

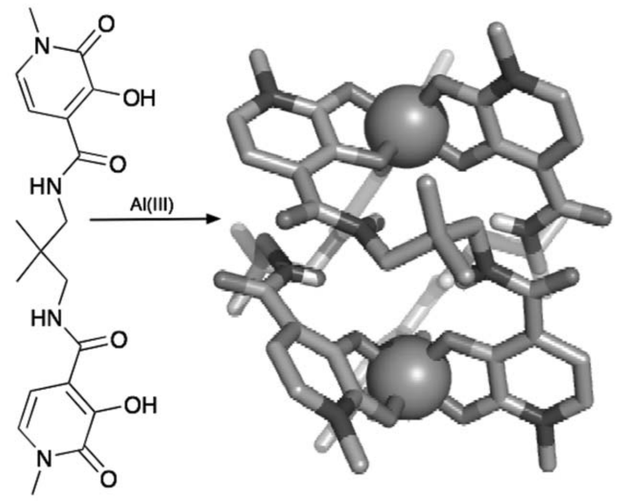

Fig. 8 Al_2L_3 helicate on right prepared from hydroxypyridinone ligand on left. The Al(III) centers are separated by 7.13 Å.

twist much less stable as a result of interligand repulsions, and thus the *meso* and helical isomers interconvert slowly.[18]

Following the pioneering work of Saalfrank in preparing the first M_4L_6 coordination cluster,[19] many groups have presented spectacular examples of related tetrahedral assemblies. The use of gallium(III) has played a crucial role in this research, as it maintains a predictable octahedral coordination geometry with hard donor ligands (such as catecholates) and the complexes are diamagnetic, enabling study by NMR spectroscopy. In this case, it is clear that main group elements can serve as effective models to study supramolecular systems when transition metals have properties (such as paramagnetism in iron catecholates) that are not conducive to the use of certain spectroscopic or characterization techniques.

Rather than survey the entire field of supramolecluar gallium coordination clusters, the reader is directed to a thorough recent review on this topic.[20] A few representative examples based on catecholate and β-diketonate ligands are reviewed here. It should be noted that many structures analogous to those prepared with Ga(III) have also been observed using In(III) instead.

In particular, dicatecholamide ligands linked with an anthracene backbone are known to form either an M_2L_3 helicate *or* an M_4L_6 tetrahedron depending on the presence or absence of a suitable cationic guest (Fig. 9). In this case, the use of the more labile Ga(III) cluster rather than a substitution-inert Ti(IV) analog was key to allow study of this interconversion process on a reasonable timescale. Phenyl, naphthyl, and pyrenyl groups have also been used to great effect as ligand spacers in preparation of these tetrahedral structure types. A large series of coordination tetrahedra based on chelation of catecholamide donors to aluminium, gallium and other main group ions has also been recently reported by Raymond and co-workers.[21] These certainly fall under the purview of main group supramolecular chemistry; however, all the coordination modes in these structures are octahedral, so we defer discussion of these structures to Section 8, where their rich host–guest is discussed in-depth.

Thallium diverges sharply from the other Group 13 elements in that it prefers a monovalent oxidation state and exhibits a much wider variety of coordination modes. Structural studies have indicated that many Tl(I) complexes display a stereochemically active lone pair which leads to hemidirected coordination geometries such as trigonal pyramidal. Tl(I) participates in a wide variety of secondary bonding interactions in the solid state, including Tl(I)···Tl(I) interactions in at least one example.

A dinuclear complex containing two Tl(I) centers coordinated to a phthalocyaninato macrocycle contains several interesting features (Fig. 10).[22] Each Tl(I) center is coordinated to four ring nitrogens and has a stereoactive lone pair, leading to a square pyramidal coordination geometry which is quite uncommon. Futhermore, a weak Tl(I)···Tl(I) interaction (dashed line) is observed through the center of the macrocycle, where the two Tl(I) centers are separated by 3.69 Å. This is slightly less than the sum of the van der Waals radii of two Tl atoms (3.92 Å). It is apparent from this and other structures

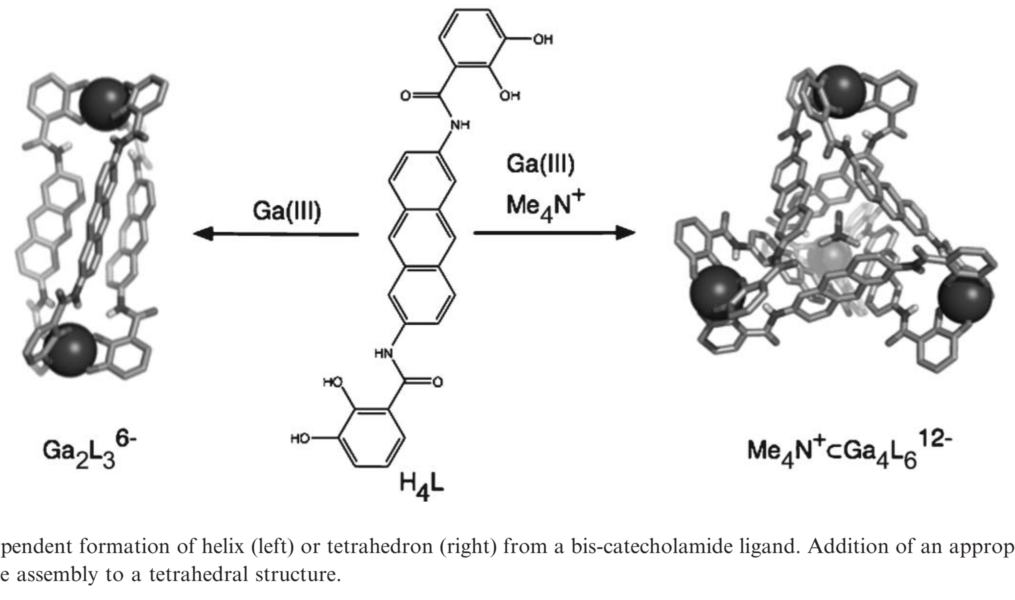

Fig. 9 Guest-dependent formation of helix (left) or tetrahedron (right) from a bis-catecholamide ligand. Addition of an appropriate guest to the helicate drives the assembly to a tetrahedral structure.

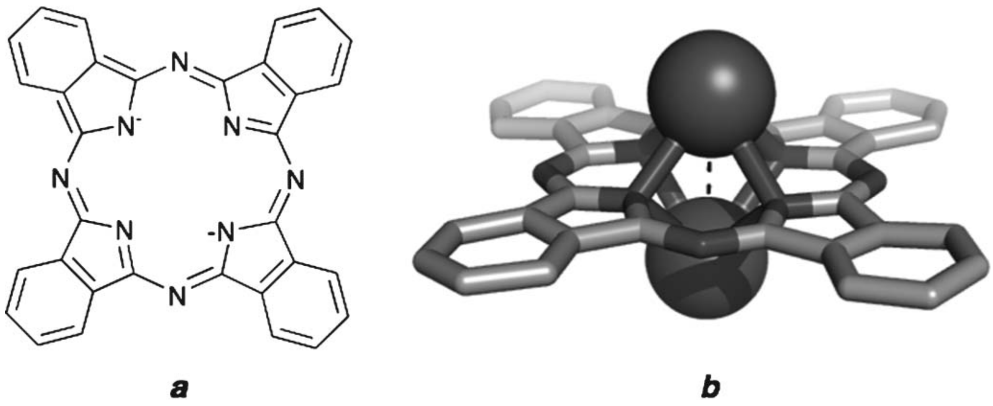

Fig. 10 Phthalocyaninato ligand (*a*) and its dinuclear Tl(I) complex (*b*). Each Tl(I) is coordinated to four nitrogen donors in a square pyramidal fashion and a weak Tl(I)···Tl(I) interaction is observed where the distance between the two metal centers is 3.69 Å.

that these weak interactions between main group ions may have important implications for the design and synthesis of main group supramolecular complexes. Their inclusion may allow for fine tuning of desirable electronic and optical properties, and these interactions alone comprise a supramolecular interaction that can be exploited as a self-assembly motif.[23]

5. Group 14—germanium, tin, and lead

The heavier elements of Group 14 (Ge, Sn, and Pb) tend toward the formation of complexes where the central atom is in the II or IV oxidation state and bears a combination of O, N, and S-donor ligands. The coordination geometries found in these complexes tend to be variable and complex. While tetrahedral and octahedral complexes are certainly observed frequently, coordination numbers can range from two up to ten, and even twelve in rare cases.[24] A deeper understanding of the coordination chemistry of these elements is desirable, especially given their well-known toxic effects and health hazards. These elements also provide interesting opportunities for ligand design, due to frequently observed stereoactive lone pairs that cause hemidirected coordination geometries.

Germanium is generally found in coordination complexes as Ge(IV) and is known to coordinate strongly to hard oxygen donors such as catecholates. In contrast to the structures observed with chalcogen donors and metals such as Al(III), Ga(III), or In(III); Ge(IV) tends toward the formation of cage-type structures of the form $[Ge_4X_{10}]^{4-}$ with X being a chalcogen donor such as sulfur or selenium.

M_4L_4 and M_4L_6 tetrahedral coordination assemblies analogous to those formed with Ga(III) and Al(III) have been reported using Ge(IV) instead (see figures in Section 8); these were prepared in order to elucidate the mechanism of guest exhange in the Group 13 assemblies, as Ge(IV) is much more inert to ligand substitution than its trivalent counterparts. Ge_4L_6 was characterized by NMR and high-resolution mass spectral techniques rather than crystallographically due to the poor quality of crystals obtained. Had guest exchange occurred *via* a partial ligand dissociation mechanism, the rate of guest exchange should have slowed relative to the Ga(III) structure when a tetravalent metal cation such as Ge(IV) was substituted. As the rate of guest exchange was unaffected, the Ge(IV) structure helped to show that the exchange mechanism involved deformation of the host.

Tin(IV) is also well known to form tris-chelate complexes with catecholate donors, leading to the design and synthesis of C_{3h} symmetric mesocates (achiral structures with both Δ and Λ centers) containing two tin ions bound to symmetry equivalent coordination sites and a second metal such as silver or palladium coordinated to the softer phosphine donors of the ligand (Fig. 11). When the mesocate is prepared using silver, a Cs(I) guest appears to mediate the structure's formation—this guest is included in the cluster's cavity and is necessary for formation (the supramolecular structure does not form in its absence).[25] This approach takes into account the hard/soft coordination preferences of both metals and allows the formation of heterometallic supramolecular structures with great site specificity.

A variety of tin-containing macrocyclic triangles derived from organotin precursors have been reported using bifunctional bridging ligands. A more thorough review of these multinuclear organotin structures has been prepared by Haiduc.[23]

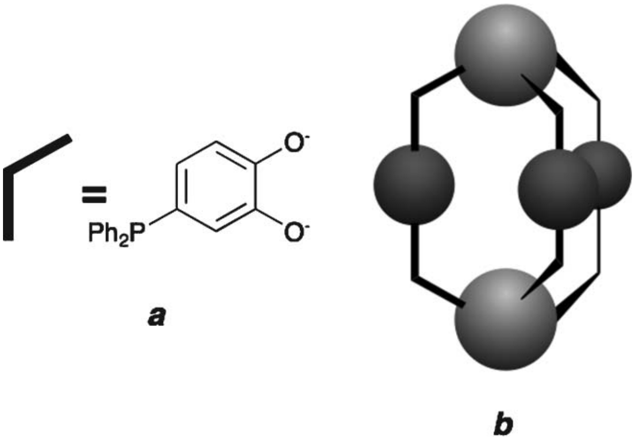

Fig. 11 A bifunctional ligand (*a*) containing catecholate and phosphine donors assembles with tin(IV) (shown as larger spheres) and either silver(I) or palladium(II) (shown as smaller spheres) to form a C_{3h} symmetric heterometallic structure.

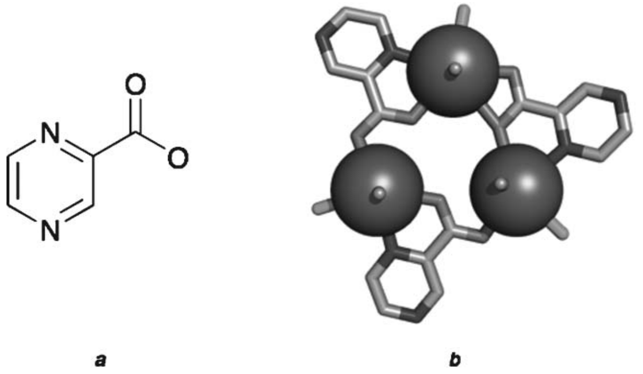

Fig. 12 Pyrazine carboxylate ligand (*a*) and supramolecular triangle (*b*) prepared from a tin(IV) precursor. Tin(IV) centers are separated by 5.35 Å.

Pyrazine carboxylic acids have also been shown by Ma and co-workers to drive the self-assembly of a trinuclear Sn(IV) macrocycle (Fig. 12).[26] These structures bear tin(IV) in a distorted octahedral geometry where the metal center is coordinated by a chelate ring containing both an oxygen and nitrogen on one ligand, as well as a carboxylate oxygen on a second ligand. Each chelating portion of the ligand is oriented at a 60° angle to the chelating group of the next ligand, which supports the formation of an equilateral triangle. It is interesting to note that the R groups on the organotin precursor have a strong effect on the crystal packing of the triangle: when R is a methyl group, all the triangles exist in an extremely close-packed structure, whereas when R is the much bulkier di-*n*-butyl group, the triangles spread out and segregate into overlapping regions of alkyl and aromatic groups in the crystalline lattice.

Many other examples of tin-containing supramolecular triangles have been prepared, a few representatve examples are discussed below. The contributions of Höpfl and co-workers illustrate the effects of solvent on the formation of larger tin-containing architectures,[27] especially in the formation of a spherical hydrogen-bonded capsule which forms an extended three-dimensional structure in the solid state. In this structure (Fig. 13), a pyridine dicarboxylate ligand (*a*) assembles with organotin precursors to form a triangle (*b*), which then forms a repeating capsular structure in the solid state (*c*), where each triangular face is shared to form a large, porous structure sustained by the presence of 36 hydrogen bonds per repeating unit.

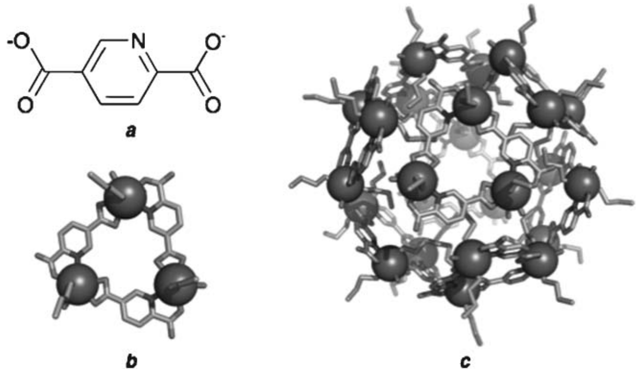

Fig. 13 A pyridine dicarboxylate ligand (*a*) assembles with organotin precursors to form the trinuclear macrocycle shown in (*b*). The extended solid state structure of this assembly forms a repeating capsular structure (*c*).

Lead(II) has appeared in several supramolecular assemblies, presumably a result of its reasonably predictable coordination preferences with certain types of ligand donors, especially those containing pyridyl nitrogens. The large size of the Pb(II) ion also provides opportunities for the synthesis of expanded structures with less steric strain than an analogous transition metal complex. Pb(II) is generally observed in distorted tetrahedral or octahedral coordination environments with a prominent stereochemically active lone pair.

A series of grid-type architectures self-assembled from linear pyridine/pyrimidine ligands and Pb(II) ions have been reported by Lehn and co-workers. This strategy is well-illustrated in a spectacular example of a self-assembled grid-type structure containing eight tetratopic, tridentate pyridine based ligands and *sixteen* Pb(II) ions, constituting a [4 × 4] grid, shown in top-down and side-on views in Fig. 14.[28] The self-assembly of this twenty-four component system containing 96 coordinate bonds overcomes enormous energetic barriers and effectively highlights the power of self-assembly in the fabrication of grid-type architectures. The structure also contains 16 closely coordinated triflate anions and 8 waters; there are a further 16 triflate anions and one additional water molecule located in secondary coordination with the structure. The ligands in the structure are bent such that the overall form is that of a saddle. The short (3.62 Å) π-stacking distances clearly contribute to the stability of this assembly. The lead(II) atoms are coordinated in a hemidirected fashion with between 7 and 9 donors depending on the number of anions associated with each.

Similar pyridine/pyrimidine ligands have induced the formation of [3 × 3] and [3 × 2] grids. Attempts to prepare even larger grids from ligands containing five chelating sites on each ligand led to the surprising formation of a dinuclear helical structure when the ligand wrapped around two Pb(II) centers separated by 3.94 Å. In the absence of Pb(II), the ligand was observed to exist in an extended, linear conformation—the helix was observed only when Pb(II) was coordinated, shown in Fig. 15. The specific folding and unfolding of an organic precursor in the presence of a metal template could have

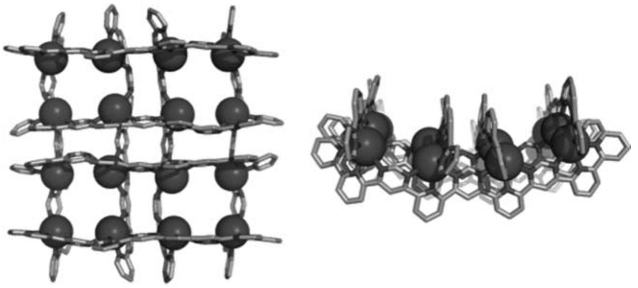

Fig. 14 $Pb_{16}L_8$ grid assembly with a "saddle"-type structure. Triflate anions and coordinated water molecules have been removed for clarity. Left: top view, right: side view. π–π stacking distance between ligands is 3.62 Å; average Pb(II)···Pb(II) distance is ∼6.5 Å.

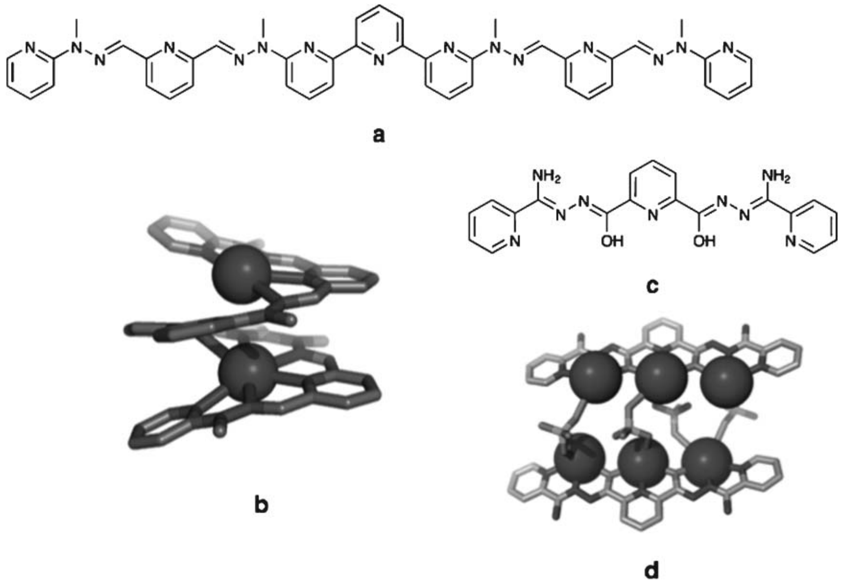

Fig. 15 Attempts to prepare larger grids from a pentatopic ligand (*a*) yielded the dinuclear Pb_2L helix (*b*). The tritopic ligand (*c*) yields two strands of Pb_3L bridged by four perchlorate anions (*d*).

promising implications for the design of functional materials that mimic biological systems.[28]

An alternate approach to preparing supramolecular structures containing Pb has focused on using ligands which bear a negative charge to balance the divalent lead(II) cation, reducing the presence of coordinating counterions. While the use of alkoxydiazine groups on the chelating site did not lead to the expected formation of a [3 × 3] grid structure, a rather fascinating hexanuclear lead(II) structure formed where three lead ions coordinated to each of two ligand strands. (Fig. 14, *c* and *d*.) The grids were then linked in the solid state by bridging perchlorate anions.[29]

6. Group 15—arsenic, antimony, and bismuth

The heavier members of Group 15, also known as the pnictogens, are particularly interesting as design elements for supramolecular main group chemistry, owing to a rare preference for a tripodal trigonal pyramidal coordination geometry found infrequently in transition metal complexes. This coordination mode is particularly attractive as a design element as the coordination vectors involved produce the vertex of a convex polyhedron. This convergent arrangement of ligands in these complexes should favor formation of discrete species without the requirement for blocking ligands often used in other supramolecular design strategies. When observed in their preferred coordination sphere, an additional stereochemically active lone pair of electrons is available: the pnictogens are well known to act as both Lewis acids and bases. In particular, the Lewis acidity of these elements increases markedly as one moves down the group: Bi(III) predominantly behaves as a Lewis acid (due to the lone pair primarily inhabiting a low energy s-orbital), while nitrogen behaves primarily as a Lewis base. This fact may contribute to the possibility for further reactivity of the pnictogen after being incorporated into a supramolecular structure. Finally, these elements are frequently involved in a variety of the weak secondary interactions that form the basis of supramolecular chemistry.[30] As the field of supramolecular pnictogen chemistry is extremely broad, we present several representative examples of the many complex types known in the literature, with relevant reviews noted as appropriate.

The tripodal coordination mode found in many arsenic–thiolate complexes has led to the facile synthesis of both As_2L_3 triple mesocates[31] and a pair of $As_2L_2Cl_2$ macrocycles[32] from *p*-dimercaptoxylene and As(III) (Fig. 16). These structures are stabilized by interactions between the arsenic lone pair and the π system of the central aromatic ring and are in fact so robust that extended heating under ambient atmosphere in the presence of competing metal ions, trifluoromethanesulfonic acid, and *p*-toluenesulfonic acid fail to cause dissociation of the assembly. Despite the remarkably robust nature of the assembly, proton NMR experiments indicate the rapid interconversion of the two macrocycles in solution. Analogous Sb_2L_3 and an $Sb_2L_2Cl_2$ macrocycle have also been reported using the same ligand.[33]

Tartrate salts are well known to form a variety of interesting structures with both As(III) and Sb(III). A dinuclear, double stranded macrocycle forms with As(III) coordinated by two hydroxylate and two carboxylate groups from each ligand, leading to a disphenoidal 4-coordinate geometry around the arsenic center, with the stereoactive lone pair maintained.[34] As tartaric acid bears two chiral carbon centers (*R*,*R*, *S*,*S*, and *R*,*S* are possible), any metal complexes arising from this ligand will have several possibilities for their overall stereochemistry. Steric arguments have been used to explain the much greater stability of assemblies containing enantiomerically pure tartrate ligands—the physical interactions between As(III) centers by way of the bridging ligand causes the chirality at each metal center to depend strongly on the other.

Antimony tartrate salts are also quite well known. Potassium antimony(III) tartrate has a long history as a

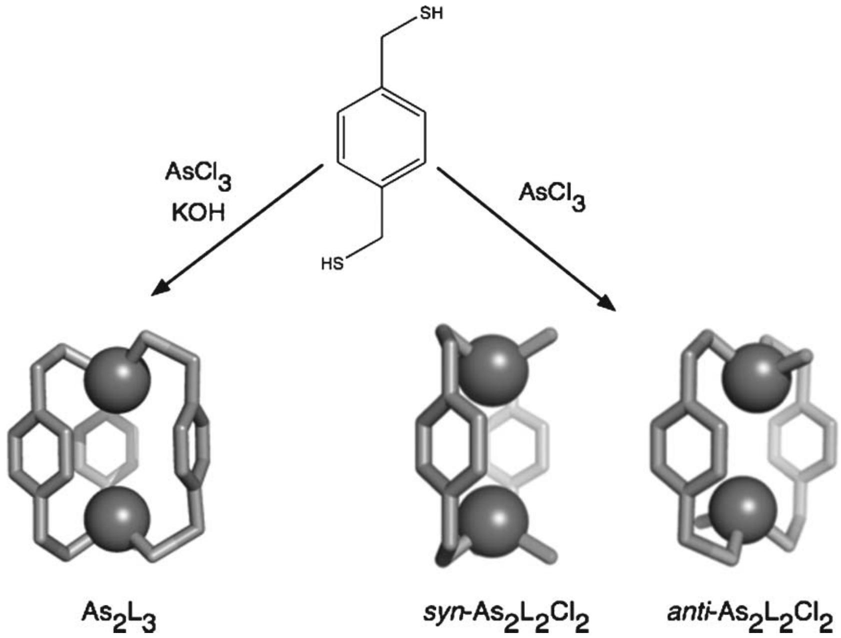

Fig. 16 α,α′-Dimercaptoxylene leads to the formation of either an As_2L_3 mesocate in the presence of base or a mixture of *syn* and *anti* $As_2L_2Cl_2$ macrocycles in the absence of base.

pharmaceutical and is in fact one of the few supramolecular complexes in widespread medical use,[35] mainly in the treatment of parasites such as those causing schistosomiasis. Interestingly, this complex was long believed to exist as a monomer until modern X-ray crystallography techniques revealed that this species is a self-assembled dinuclear macrocycle. As was observed with As(III), the Sb(III) centers are coordinated to two hydroxylate and two carboxylate oxygen donors, leading again to a disphenoidal coordination sphere. Furthermore, these Sb(III) tartrate complexes are only known to form from (*R*,*R*) or (*S*,*S*) combinations; a mixed macrocycle containing both tartrate enantiomers does not form. *Meso*-tartrate complexes containing the (*R*,*S*) isomer of tartrate are also unknown. Even more interestingly, when Sb(III) and As(III) are combined and added to the tartrate salt, mixed macrocycles containing one of each metal center form, which reinforces the idea that these macrocycles form through genuine self-assembly processes and concomitant rearrangement of weak metal–ligand bonds.[36]

The pnictogens are also known to assemble with a variety of organic and inorganic components to form cyclic oligomers. One example (Fig. 17) involves the formation of an Sb_6Na_6 alternating ring, supported by the presence of 3-methylcatecholate and coordinated THF molecules.[37] As(III) and Sb(III) complexes can also both assemble with Group 13 elements such as Ga to form cyclic oligomers.[38] Alternating structures of these types may lead to use as interesting precursors for the preparation of semiconductor materials. The ring-like structures are often prepared through reactions which include salt or alkane elimination, as well as dehalosilylation reactions.

As Bi(III) compounds are often challenging to handle due to undesirable properties such as the ease of formation of insoluble oxide salts, its supramolecular chemistry is not nearly as well-developed as is that of As(III) and Sb(III). However, due to its unique position in the periodic table as the heaviest nonradioactive element, it has some important differences in coordination and reactivity from the rest of the Group 15 elements. A large atomic radius and the availability of expanded orbitals leads to a more variable coordination sphere; coordination numbers as high as 9 and 10 have been observed. Because of this fact, for example, tartrate complexes of Bi(III) (used in medicine to treat syphilis) tend to form polymeric structures with coordination number five (instead of four as observed with the lighter pnictogens) in order to satisfy its greater coordination demands.

A few notable examples which illustrate the intriguing coordination chemistry of Bi(III) are discussed here. Thiosalicylic acid and Bi(III) form an octanuclear complex where a ring of six Bi(III) centers are supported by coordination to six oxygens and one sulfur atom, while two additional bismuth atoms lie above and below the ring's center and are bound by three sulfur and three oxygen atoms. The "empty

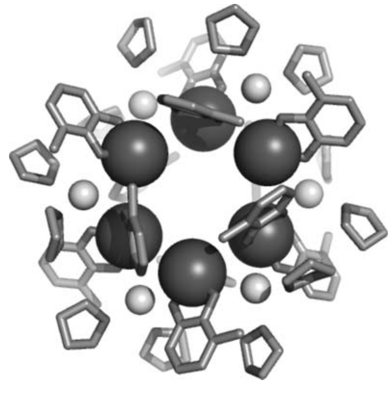

Fig. 17 Hexanuclear Sb(III) ring structure formed from 3-methylcatecholate ligands, with alternating Na(I) cations and coordinated THF molecules. Sb(III) is shown as larger spheres, while Na(I) is shown as smaller spheres.

spaces" of the coordination spheres on the two Bi(III) atoms point into the cavity formed by the ring, possibly forming a secondary Bi–Bi interaction.[39]

Finally, it has been shown that the high coordination number preferences of Bi(III) can be side-stepped by the use of a multidentate capping ligand which leaves only a few coordination sites available for the coordination of bridging ligands. This approach has been used to prepare a dinuclear Bi(III) macrocycle—triazacyclononanes are used to cap the Bi(III) centers through their nitrogen groups, while the carboxylate group bridges to the second Bi(III) center.[40]

7. Group 16 and 17—chalcogens and halides

In general, elements of Group 16 and 17 have not found widespread use as building blocks for supramolecular architectures. The heavier chalcogens in Group 16 such as selenium and tellurium do provide some notable exceptions. These elements are commonly found in the (II) or (IV) oxidation states and their secondary interactions with the halogens have been well-documented in model systems.[41] Tellurium(IV) has also been shown to form a trinuclear Te_3L_3 macrocycle (L = 1,2-benzenedicarboxylate) with two *p*-tolyl supporting ligands (Fig. 18).[42] The Te(IV) cations are arranged in an equilateral triangular fashion with an average Te(IV)···Te(IV) distance of 6.30 Å. The coordination geometry around each Te(IV) center is slightly distorted from an ideal disphenoidal structure: the O–Te–O bond angle averages 168.3°, while the C–Te–C angle averages 98.5°. While this structure may be categorized as organometallic due to the presence of Te–C bonds, the macrocyclic structure itself is supported by the assembly of the dicarboxylate ligands.

In a particularly elegant example of synthetic fabrication, Stang and co-workers prepared a molecular square $[I_4L_4]^{4+}$ containing iodinium cations in their *cis*-square-planar arrangement and a linear biphenyl group as the organic linker.[43] As direct crystallographic observation was not possible with this assembly, based on ESI-MS and NMR data, an energy-minimized model was prepared (Fig. 19).§ While this molecular square should perhaps not be considered a true supramolecular or self-assembled structure due to the stepwise nature of its synthesis, it is nonetheless an excellent and illustrative example of a main group element being used to direct the formation of a nanoscale structure.

It is clear from the few examples of Group 16 and 17 supramolecular structures that these elements provide interesting motifs for the construction of supramolecular assemblies; the unique manner in which these elements can bind to organic groups will likely expand the variety of structures containing main group elements in the future.

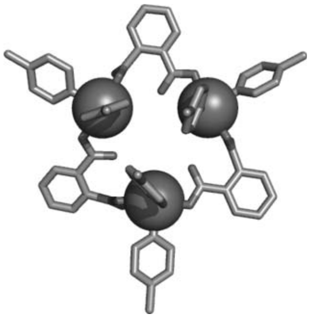

Fig. 18 Supramolecular triangle based on coordination of dicarboxylates to organotellurane centers. The average distance between Te(IV) centers is 6.30 Å.

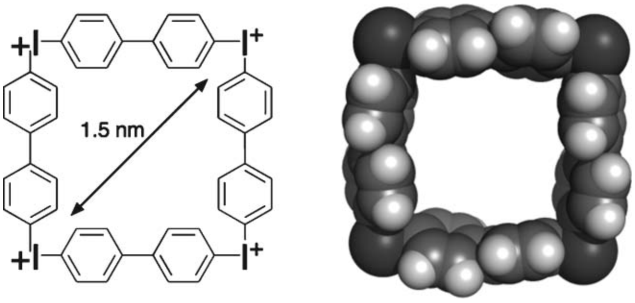

Fig. 19 A molecular square based on coordination of biphenyl bridges to *cis*-square planar iodonium cations. A schematic view is shown on the left; a space filling molecular model is on the right. The diagonal distance across the square is approximately 1.5 nm.

8. Host–guest chemistry of supramolecular main group complexes

As research in main group supramolecular chemistry is less developed than in transition metal-based supramolecular chemistry, likewise the host–guest chemistry of the main group congeners is less explored as well. Many of the structures described have host cavities of insufficient size or inappropriate shape to contain common guest molecules. Additionally, the electronic properties of main group elements often vary substantially from those of the transition metals, which may affect the nature of the host structure's cavity in a manner precluding the entry of a guest molecule. A notable example is the As_2L_3 structure described in Section 6: all efforts to bind small guests or metal ions (even protons) in the cluster cavity have failed. Without a more spacious cavity, this assembly appears to be devoid of host–guest chemistry.

In contrast, both the Ga_4L_6 tetrahedra[21] prepared by Raymond and co-workers and the mercuracarborands prepared by Hawthorne[15] have exhibited a wide variety of rich host–guest chemistry which has led to a greater understanding of the solution phase behavior of supramolecular assemblies. A combination of NMR studies and computer calculations of tetrahedra containing a variety of metal centers has revealed the mechanism for guest exchange in these structures. Guests escape the cavity through a deformation of the host structure which permits guests to enter and exit through existing apertures, rather than *via* partial dissociation of one or more

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§ The computer model reported by Stang and co-workers featured the biphenyl linkage in a completely coplanar conformation rather than the conformation in which the rings are twisted at a 30 degree angle to one another. In the computer modelling performed to generate a structure for Fig. 18, we were unable to reproduce this coplanar conformation, a fact that could be attributed to differences in modelling software (HyperChem in the Stang report, compared with CAChe in this treatment). All molecular models in this work were prepared using Fujitsu's CAChe 5.0 software using the MM3 basis set.

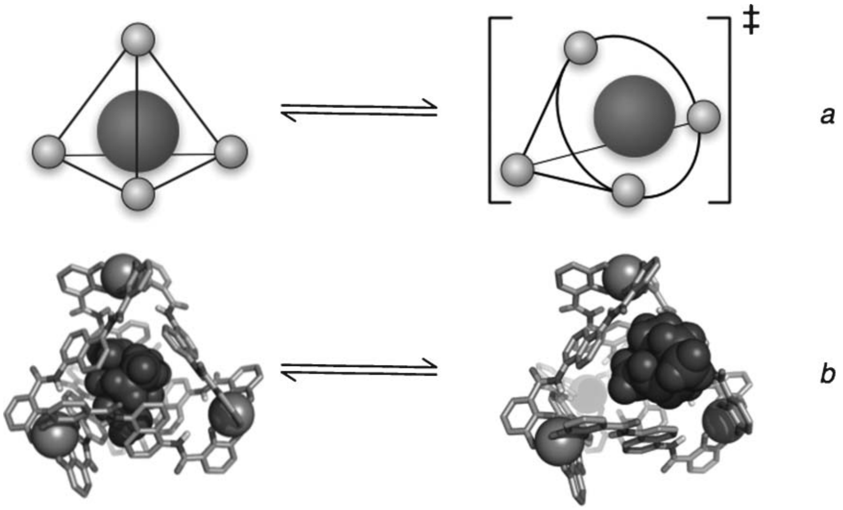

Fig. 20 Mechanism for guest exchange from M_4L_6 host structures showing host distortion. (*a*) Cartoon representation. (*b*) Molecular model representation.

ligands from one of the metal center vertices (Fig. 20). For example, guest exchange rates were comparable when the tetrahedra were assembled from Ge(IV) or Ga(III). Ge(IV) is more inert to ligand substitution than Ga(III); therefore, it could be inferred that partial ligand dissociation was not a significant factor in guest exchange. Molecular modelling corroborated this. It was shown that an aperture of sufficient size for ingress and egress of guest molecules could be formed through only deformation of the host structure. Furthermore, a cleverly designed amphiphilic guest containing a Ru(III) sandwich complex and an alkylsulfonate tail can enter through one host aperture without disrupting the structure, leaving the "tail" of the guest outside the cavity, as illustrated in Fig. 21. This may have significant implications for applications in catalysis or synthesis of linear polymers in a stepwise fashion inside a properly designed nanoscale reaction vessel.

The mercuracarborands described previously also show rich anion-binding properties, especially with the halides.[15] For example, the formation of [12]mercuracarborand-4 requires the presence of a halide template; in its absence, the smaller and less strained [9]mercuracarborand-3 forms instead (Fig. 6). Furthermore, it has been shown that the iodide guest may be removed from the tetranuclear host with silver acetate; the resulting empty macrocycle loses its planar structure and adopts a folded "butterfly" conformation. This now-empty host has been shown to complex both nitrate anions as well as $B_{10}H_{10}^{2-}$.

The trinuclear macrocyclic host has been involved in the formation of several interesting sandwich-type structures, such as a 2 : 1 carborand : benzene structure observed in the solid state. Hexamethyl-[9]mercuracarborand-3 also forms 2 : 1 complexes with halide ions (Fig. 22). The halide is coordinated to six Hg(II) centers, forming what is thought to be three equivalent three-center, two-electron bonds between the anion and each macrocycle. This is supported by the decreasing distance between the trimer planes with decreasing guest size and the equidistant mercury-halide atoms which were less than the sum of the van der Waals radii.

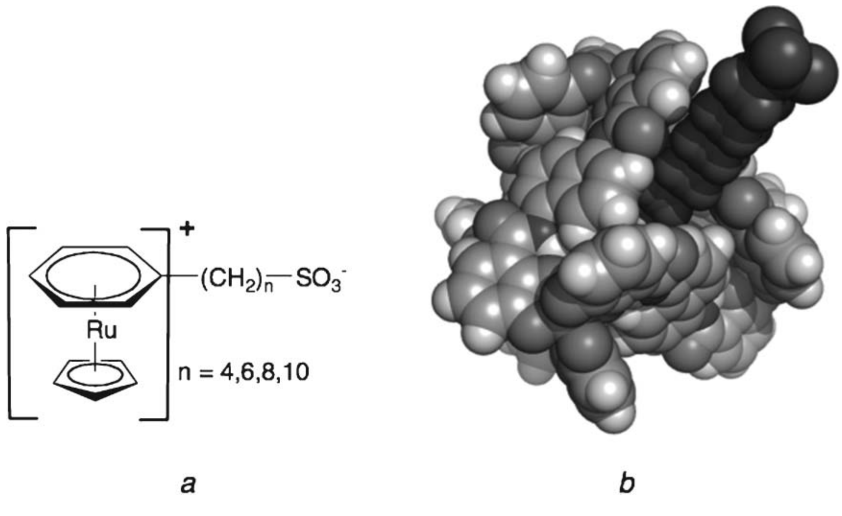

Fig. 21 Partial encapsulation of an amphilic guest molecule. Ru(III) sandwich complex (*a*) with alkylsulfonate tail encapsulated at the hydrophobic end; (*b*) the hydrophilic sulfonate head group exposed.

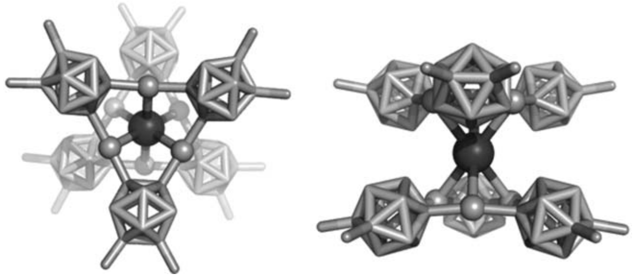

Fig. 22 Halide sandwich complexes of hexamethyl-[9]mercuracarborane-3. View from top is shown at left; side view at right. The halide shown is iodide—similar complexes form from both chloride and bromide. The distance between Hg–macrocycle planes is I^- (4.90 Å) > Br^- (4.764 Å) > Cl^- (4.672 Å).

Conclusions

The main group elements have been used to prepare a wide variety of supramolecular, self-assembled structures. Many of these structures contain geometric elements which are either inaccessible or require use of blocking ligands when using transition metals as directing groups. While the main group elements have certainly not seen the widespread use in supramolecular chemistry enjoyed by the transition metals, it is clear that there is much utility to be found in this section of the periodic table, particularly in situations where the properties of a transition metal might preclude the use of a desired experimental technique. This has been particularly important in studying the solution state behavior of catecholamide-based supramolecular structures. The paramagnetism of iron(III) prevents study of these clusters by NMR. Gallium(III), on the other hand, served as an extremely effective model for these systems, allowing for more rigorous characterization of the supramolecular structures and dynamics. As more is understood about the supramolecular coordination chemistry of the main group elements, more and larger structures will continue to be prepared. We anticipate that these structures will see novel uses in the design and synthesis of functional materials and perhaps as synthons for materials for optics, electronics, and other emerging fields. One must also note that there are many challenges associated with work in the main group—coordination geometries are often unpredictable and can lead to unexpected difficulties with solubility or characterization. Crystalline samples of these large structures are also at times difficult to prepare and one must rely on combinations of solution techniques to characterize products. Nevertheless, the stability imparted by self-assembly can lead to robust main group complexes. Given the interest in Bi-containing radiopharmaceuticals and other applications of main group chemistry, supramolecular structures such as those describes herein may find application in a broad range of fields.

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