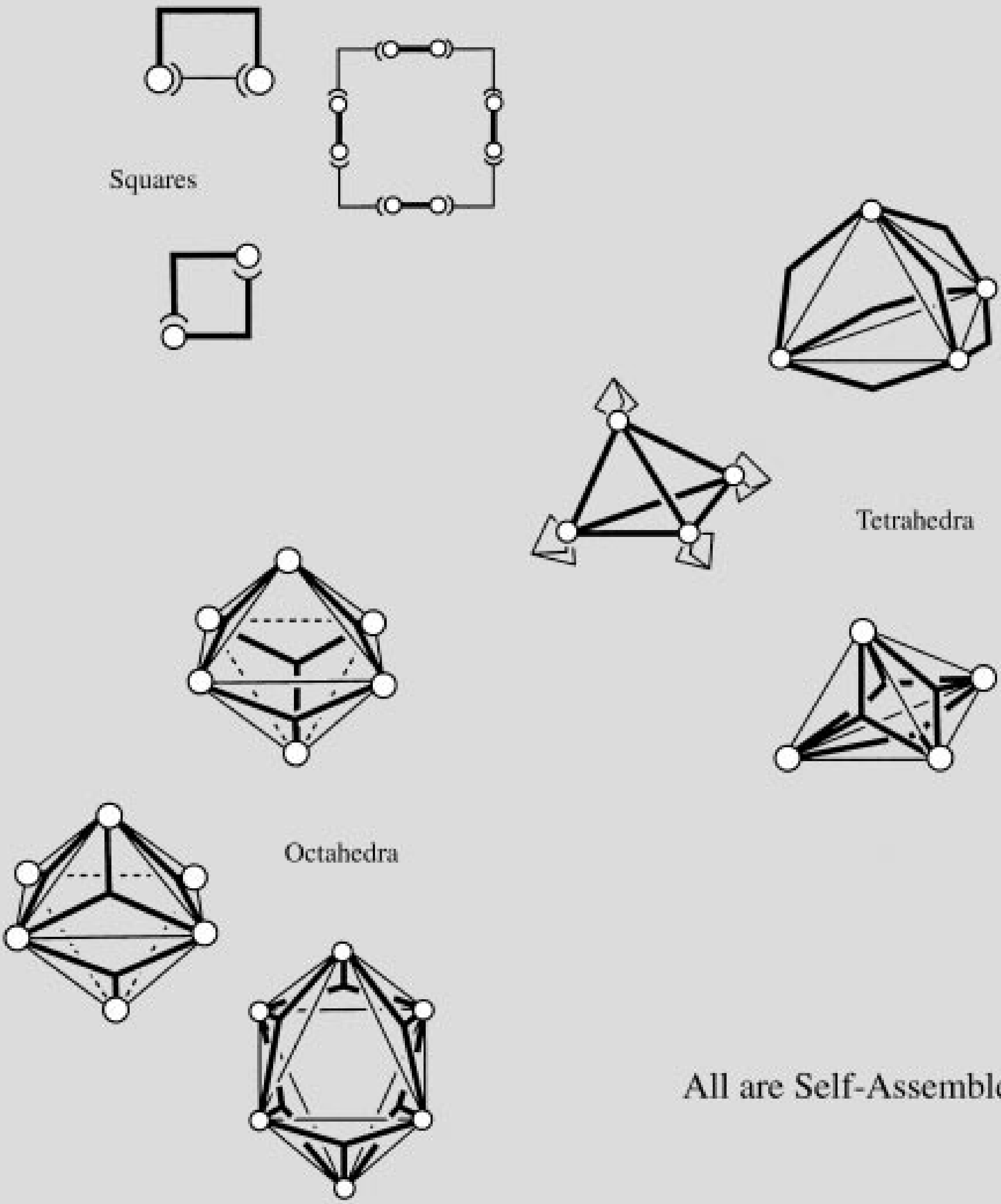
Metal-Containing Molecular Containers

What do they have in common ?



All are Self-Assembled

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Classification of Coordination *Polygons* and *Polyhedra* According to Their Mode of Self-Assembly

Gerhard F. Swiegers*[a] **and Tshepo J. Malefetse**[a, b]

Abstract: This work extends techniques for the controlled formation of synthetic molecular containers by metal-mediated self-assembly. A new classification system based on the self-assembly of such species is proposed. The system: 1) allows a systematic identification of suitable acceptor–donor combinations, 2) widens the variety of design possibilities available, 3) allows a ready comparison of the self-assembly of different compounds, 4) reveals useful commonalities between different compounds, 5) aids in the development of novel architectures, and 6) permits identification of systems capable of being switched back-and-forth between architectures.

Keywords: coordination chemistry · metallocycles · molecular devices · self-assembly · supramolecular chemistry

Introduction

Coordination chemistry increasingly features polymetallic compounds having highly ordered and potentially useful structures. Many such compounds are prepared by the spontaneous self-assembly of discrete metals and ligands into stable, noncovalently joined coordination compounds. A variety of molecular architectures have been obtained in this way. Among the best known are the so-called metallocyclic *polygons* and *polyhedra*.[1] Complexes displaying these structural motifs have discrete, closed, two-dimensional (2D) (polygonal) or three-dimensional (3D) (polyhedral) structures which closely resemble well-known geometric shapes, including triangles, squares, hexagons, cubes, triangular prisms, and octahedra. Such materials are interesting as artificial, molecular-scale containers or receptors, in which novel synthetic chemistry, electrochemistry, magnetochemistry, photoluminescent chemistry, supramolecular chemistry, or catalytic chemistry, inter alia, can be carried out.[2]

Extensive efforts have been made to rationalize and systematize the assembly of metallocyclic polygons and polyhedra in order to allow the deliberate formation of desired architectures. The approach most commonly employed involves starting with the overall shape of the desired container and then retrosynthetically determining the geometric and symmetry properties necessary in the combinant building blocks. A rational selection of the interacting units is then possible. The symmetry properties can be determined using the so-called *Symmetry-Interaction* method recently described by Raymond and co-workers.[3] A modular assembly technique—the so-called *Molecular Library* method of Stang and co-workers[4]—is available to facilitate the choice of geometrically suitable building blocks. While this field is still in its infancy, these combined technologies have already generated several interesting new classes of polygons and polyhedra, some with near-complete geometric and dimensional control.[1]

While theoretically powerful, this overall approach nevertheless has some important limitations. It does not, for example, consider the complete range of pathways by which a particular architecture may be self-assembled, nor does it identify the best starting point for such an endeavor. Moreover, it does not reveal pertinent relationships between proposed assembly methods and comparable processes previously employed. Yet such relationships could reveal simpler, more effective ways of generating the desired architecture.

This concept article describes a new classification system for coordination polygons and polyhedra, based on their mode of self-assembly, which aims to overcome these limitations. The new system is not intended to supersede the current shape-based approach, but rather underpins it in a complementary fashion.

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Categorization of Coordination Polygons and Polyhedra According to Their Overall Shape and Its Limitations

Because it is so obvious and important, the overall shape of coordinative polygonal and polyhedral molecular containers has hitherto served as the sole means of their description. Most recently, Atwood and MacGillivray have formalized the classification of molecular polyhedra by cataloging their structural motifs in terms of their resemblance to Platonic, Archimedean, prismatic, and antiprismatic solids, and to irregular solids.[5] This approach is useful because such solids serve as convenient models of spheroidal or pseudo-spheroidal design. In addition, the Symmetry-Interaction and Molecular Library techniques make any of these structures theoretically accessible.

However, by focusing on the end-product, this classification system does little to elucidate the self-assembly options available to generate the final product. This is important because clusters of a particular shape can usually be prepared in several different ways. Moreover, a particular architecture may be readily, but not obviously, obtainable using a known self-assembly method or by a minor modification of such a process. Identical self-assembly processes can generate quite different product architectures depending on the structure of the ligands and metals employed.

From a self-assembly point of view, the shape-based classification system therefore has two distinct limitations: 1) it does not distinguish between differences in the self-assembly of ensembles having the same overall shape, and 2) it gives no indication of commonalities in the self-assembly of ensembles having different overall structures.

Point 1) can be illustrated by the fact that molecular squares can be prepared by several routes, including any one of those shown in Figure 1a–c. Except for the fact that all of these involve at least one right-angled building block, defining an assembly as a square does not provide substantive information about its self-assembly. Yet such information could be important if one were, for example, wishing to obtain a square of particular symmetry or dimensions.

Point 2) can be illustrated by considering clusters having several metal ions arranged in a particular geometry about a central cavity. Figure 2 depicts three representative polyhedra containing four tritopic metal ions. Despite their different overall shapes, all involve a *tetrahedron* of metal ions about the central cavity. A similar commonality can be seen in the two representative polyhedra depicted in Figure 3a and b. Both involve an approximate *octahedron* of metal ions about the central cavity despite quite different overall architectures.

Recognizing such relationships can be important. For example, Figure 3 shows how the latter commonality can be used to conceptualize a new architecture. A progression in topicities and stoichiometries exists in going from Figure 3a to b. Figure 3a depicts a *truncated tetrahedron* containing six ditopic ions and four tritopic ligands.[6] Figure 3b depicts a *cylinder* containing six tritopic ions and six tritopic ligands.[7] By extending the progression, that is, by combining six tetratopic metal ions with eight tritopic ligands, one obtains a discrete cluster having the overall *octahedron* architecture illustrated in Figure 3c.[8] Despite their apparently different overall shape, these three polyhedra are rather closely related from a self-assembly point of view; all have M_6L_x formulae (M = metals, L = ligands, $x = 4, 6, 8$).

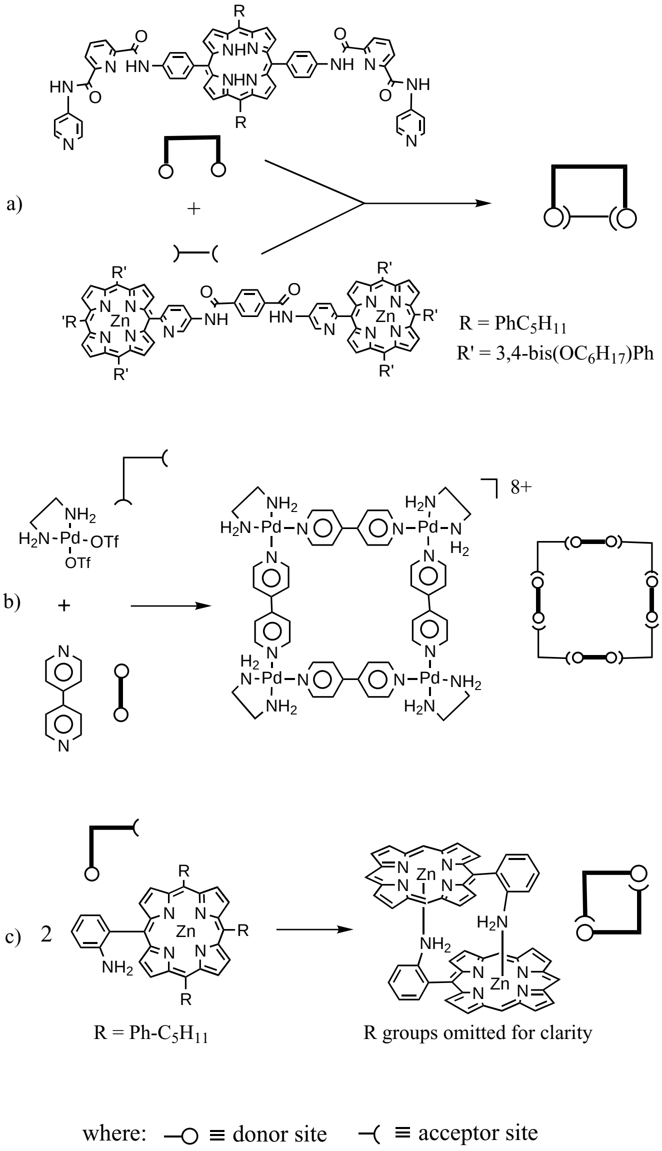

Figure 1. Selected methods for the preparation of molecular squares.[2, 15, 16] The squares have the following classifications based on the assembly descriptor classification proposed here; a) $L^{2a}_{1}A^{2d}_{1}$, b) $A^{2a}_{4}L^{2d}_{4}$, and c) A^{1a1d}_{2}. Numerous other combinations of synthons exist for the formation of squares (see Table 2). OTf = triflate = OSO_2CF_3.

A comparison of the topicities and stoichiometries of the building blocks in polygonal or polyhedral clusters can illuminate other useful relationships as well. For example, truncated tetrahedra (e.g. Figure 3a), being M_6L_4 species, are related to edge-bound M_4L_6 species such as adamantanoids (e.g. Figure 2a) by an interchange of metals and ligands. Thus, like M_4L_6 adamantanoids, M_6L_4 truncated tetrahedra also typically exhibit the rare T point group symmetry in solution.

Commonalities like those described above clearly offer valuable insights into the preparation of novel cluster architecture or the preparation of known cluster architecture by new pathways. The need for a coherent classification

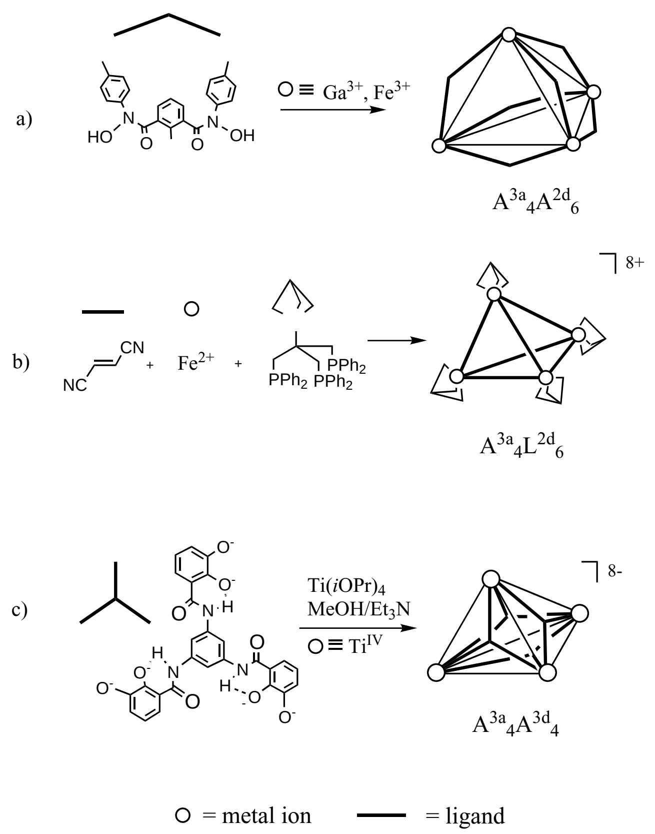

Figure 2. Schematic depiction of the structure and formation of molecular polyhedra containing four tritopic metal ions (open circles) in a tetrahedral arrangement about a central cavity; a) an edge-occupied adamantanoid, b) an edge-occupied tetrahedron, and c) a face-occupied tetrahedron.[17–19] The proposed assembly descriptor classification is given below each cluster.

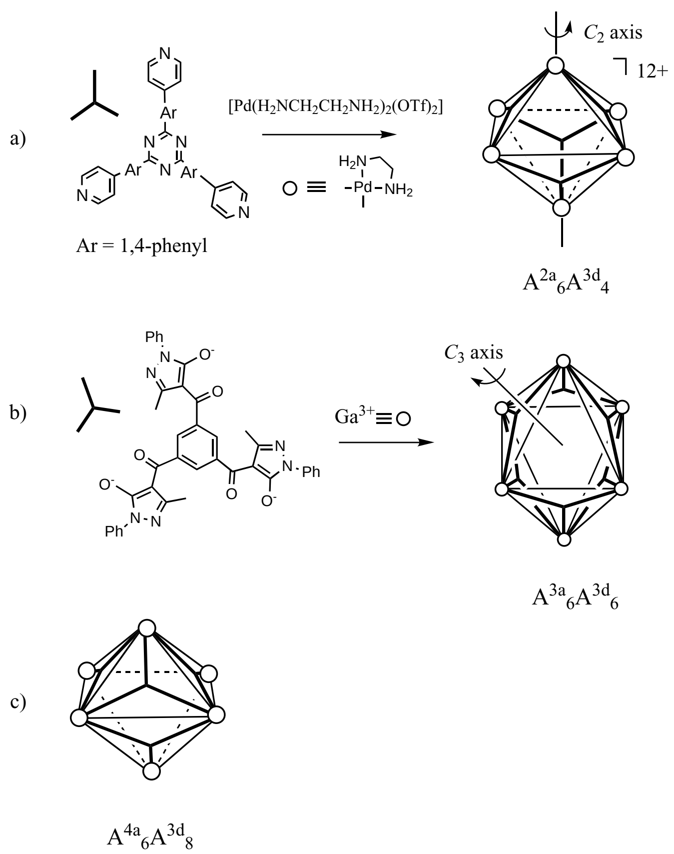

Figure 3. Schematic depiction and formation of face-bound molecular polyhedra containing six metal ions (open circles) in an octahedral arrangement about a central cavity; a) a truncated tetrahedron,[20] b) a type of molecular cylinder,[7] and c) a molecular octahedron.[8] The proposed assembly descriptor classification is given below each cluster.

system which readily reveals such relationships has been implicitly acknowledged in several earlier studies.[1a, 3, 9, 10]

To overcome the limitations of the shape-based approach, it is necessary to devise a complementary classification system which: 1) uniquely describes each self-assembly process in a way that 2) readily illustrates commonalities between different assembly processes.

Classification of the Self-Assembly of Coordination *Polygons* and *Polyhedra* by Using Modified Assembly Descriptors

The most common descriptor methodology for the self-assembly of polygonal and polyhedral coordination compounds is one originally proposed by Stang.[4] In this approach the building blocks are considered to be either rigidly linear, L, (i.e. subtending an angle of 180° between binding sites) or rigidly angular, A (i.e. subtending an angle of less than 180° between binding sites). The assembly is then denoted by subscripting the number and superscripting the topicity of each building block involved. A discrete structure formed by two tritopic angular units and three ditopic linear units is therefore symbolized $A^3_2L^2_3$. The assemblies depicted in Figure 1a–c have the Stang descriptors $L^2_1A^2_1$, $A^2_4L^2_4$, and A^2_2, respectively.

While this method provides a useful abbreviation of the self-assembly process, it does not give a unique description. However it can be readily modified to achieve this. If each of the building blocks is further superscripted with lower case "d"'s or "a"'s to indicate the types of binding site present (a "d" signifies a donor site and an "a" an acceptor site), then a unique descriptor is obtained which can form the basis for a comparative classification system.

For ease of use, the modified descriptors need to be uniformly formulated. The following conventions are employed in this work. Identical binding sites on the same building block are combined into a single "a" or "d" with a preceding numeral to indicate the number of these sites. Nonidentical sites are designated separately. Thus, the angular building block at the top of Figure 1a contains two identical donor sites and is symbolized A^{2d}. By contrast, the sole building block in Figure 1c has two, nonidentical binding sites, one a donor site and the other an acceptor site; it therefore has the descriptor A^{1a1d}. To easily compare different modes of assembly, it is also necessary to standardize the order in which the building blocks are listed in the assembly descriptor. For convenience we will use the convention that acceptor building blocks (i.e. metal-containing units) are listed first followed by hybrid building blocks (which contain both acceptor and donor sites), and, finally, by building blocks incorporating only donor sites. Where several donor or acceptor building blocks are present, these are listed in order of *decreasing topicity.* The squares shown in Figure 1a–c consequently have the descriptors $L^{2a}_{1}A^{2d}_{1}$, $A^{2a}_{4}L^{2d}_{4}$, and A^{1a1d}_{2}, respectively. Table 1 lists and groups all previously prepared coordination polygons and polyhedra according to their assembly descriptor notation; a comprehensive review describing each of these species in terms of the new system and listing their literature references will be published elsewhere.[21]

Since the assembly descriptors aim to describe the manner in which a series of separate building blocks spontaneously form a polygon or polyhedron, it should be noted that the nature of the binding at each link between the building blocks is not described. Thus, the reaction of a bidentate chelate (a donor-based binding site) with a ditopic metal ion (an acceptor-based binding site) constitutes the formation of a single link despite the fact that it involves two coordinate bonds. The descriptors also do not necessarily indicate the total number of metals or ligands present in an assembly. The classification system is, nevertheless, the only way to uniformly compare—from a self-assembly perspective—the wide variety of molecular polygons and polyhedra known. It can, additionally, be extended to the classification of molecular containers formed or partially formed using other noncovalent links.

Table 1. Assembly descriptors of known coordination polygons and polyhedra, and their molecular architecture.

Assembly descriptor	Molecular architectures
A^{1a1d}_{2}	squares
A^{1a1d}_{3}	triangles, “tricorns”
A^{1a1d}_{4}	squares
A^{1a1d}_{6}	hexagons
$A^{2a}_{1}A^{2d}_{1}$	squares
$A^{3a}_{1}A^{3d}_{1}$	cages
$A^{2a}_{2}A^{2d}_{2}$ (2D)	rhomboids, squares
$A^{2a}_{2}A^{2d}_{2}$ (3D)	cyclophane boxes, helicates
$A^{2a}_{2}A^{1a2d}_{2}$	squares
$L^{2a}_{2}A^{2d}_{2}$	squares
$A^{3a}_{2}A^{2d}_{3}$	cyclophane boxes
$A^{3a}_{2}A^{1d1d}_{2}L^{1d}_{2}$	squares
$A^{2a}_{3}A^{2d}_{3}$	triangles, hexagons
$A^{2a}_{3}L^{2d}_{3}$	triangles, hexagons
$L^{2a}_{3}A^{2d}_{3}$	triangles, hexagons
A^{2a}_{3} A^{3d}_{2}	cyclophane boxes
$A^{2a}_{4}A^{2d}_{4}$	square/star
$A^{2a}_{4}L^{2d}_{4}$	squares, rectangles
$L^{2a}_{4}A^{2d}_{4}$	squares, nanosquares
$L^{2a}_{4}A^{1a2d}_{4}$	square
$A^{3a}_{4}A^{2d}_{6}$	adamantanoids, tetrahedra, boxes
$A^{3a}_{4}L^{2d}_{6}$	tetrahedra
$A^{3a}_{4}A^{3d}_{4}$	tetrahedra
$A^{2a}_{4}A^{4a}_{2}A^{1d1d}_{8}$	rectangular boxes
$A^{2a}_{4}A^{8d}_{1}$	rectangular boxes
$A^{4a}_{4}L^{4d}_{4}$	rectangular boxes
$A^{2a}_{6}L^{2d}_{6}$	hexagons
$L^{2a}_{6}A^{2d}_{6}$	hexagons
$A^{2a}_{6}A^{3d}_{4}$	truncated tetrahedra
$A^{2a}_{6}A^{3d}_{6}$	cylinder
$A^{2a}_{6}A^{3d3d}_{2}$	hexagonal box
$A^{2a}_{6}L^{3d}_{2}L^{2d}_{3}$	cylinders
$A^{2a}_{9}L^{3d}_{3}L^{3d}_{3}$	cylinders
$A^{2a}_{12}L^{4d}_{3}L^{3d}_{4}$	cylinders
$A^{4a}_{6}A^{2d2d}_{6}$	hexagon
$A^{4a}_{8}A^{2d2d}_{8}$	octagon
$L^{2a}_{8}A^{1a2d}_{8}A^{2d}_{4}$	rectangular box
$A^{3a}_{8}L^{2d}_{12}$	cubes
$A^{3a}_{8}A^{2d}_{12}$	cuboctahedra
$L^{2a}_{12}A^{1a4d}_{1}A^{1a3d}_{4}A^{1a2d}_{4}$	square array
$L^{2a}_{12}A^{1a4d}_{1}A^{1a3d}_{4}A^{1a2d}_{4}L^{2d}_{9}$	square array sandwich
$A^{2a}_{18}A^{6d}_{6}$	hexahedra
$A^{3a}_{20}L^{2d}_{30}$	dodecahedra

The Application and Advantages of the Classification System

Systematic analysis of self-assembly pathways leading to a particular polygon or polyhedron: One way of using the new system involves a systematic analysis of the self-assembly pathways which can theoretically lead to a desired polygon or polyhedron. The most common locations of the individual building blocks in molecular polygons and polyhedra are the corners, edges and faces of the structure.[4] Thus, in a two-unit assembly, one building block may occupy the corners and the other the edges or faces of the structure. Alternatively, one unit may occupy some of the edges or corners, while the other occupies the rest. Permutations of these and other possibilities give all the possible combinations of building blocks which could generate a particular structure. Table 2 lists an illustrative set of assembly descriptors available for the formation of three representative and symmetrical molecular polygons involving one or two building blocks—triangles, squares, and hexagons. Because a polygon has only one face and it needs to be open to act as a host, only permutations involving corners and edges are typically available. The corners of polygons must generally be occupied by acceptor or donor units since coordinate bonding cannot occur at an angle. The edges of polygons may, however, be formed by units formally located on the corners, so that descriptors exist in which the edges appear to be unoccupied; for example, A^{1a1d}_{2} for the square illustrated in Figure 1c.

Table 2. Illustrative list of possible descriptors for the assembly of symmetrical molecular *polygons* containing one or two building blocks. The occupation of corners and edges by acceptor (a) or donor (d) building blocks is listed, along with the assembly descriptors which result.

	Corners occupied	Edges occupied	Assembly descriptors
square	4a	4d	$A^{2a}_{4}L^{2d}_{4}$
	4d	4a	$L^{2a}_{4}A^{2d}_{4}$
	2a & 2d	–	$A^{2a}_{2}A^{2d}_{2}$
	1a & 1d	–	$A^{2a}_{1}A^{2d}_{1}$, $A^{2a}_{1}L^{2d}_{1}$
	self-cyclized		A^{1a1d}_{4}, A^{1a1d}_{2}
triangle	3a	3d	$A^{2a}_{3}L^{2d}_{3}$
	3d	3a	$L^{2a}_{3}A^{2d}_{3}$
	self-cyclized		A^{1a1d}_{3}
hexagon	6a	6d	$A^{2a}_{6}L^{2d}_{6}$
	6d	6a	$L^{2a}_{6}A^{2d}_{6}$
	3d & 3a	–	$A^{2a}_{3}A^{2d}_{3}$
	2a & 2d	–	$A^{2a}_{2}L^{2d}_{2}$, $L^{2a}_{2}A^{2d}_{2}$
	1a & 1d	–	$A^{2a}_{1}A^{2d}_{1}$
	self-cyclized		A^{1a1d}_{6}, $A^{1a1d}_{3,}$ A^{1a1d}_{2}

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Table 3 lists a similarly illustrative set of assembly descriptors for two representative molecular polyhedra, a *tetrahedron* and a *cube*. In polyhedra the building blocks may occupy faces, as well as corners and edges. Because of the many possibilities available, certain of these elements need not appear occupied at all.

Table 3. Illustrative list of possible descriptors for the assembly of symmetrical molecular *polyhedra* containing one or two building blocks. The occupation of corners, edges and faces by acceptor (a) or donor (d) building blocks is listed, along with the assembly descriptors which result.

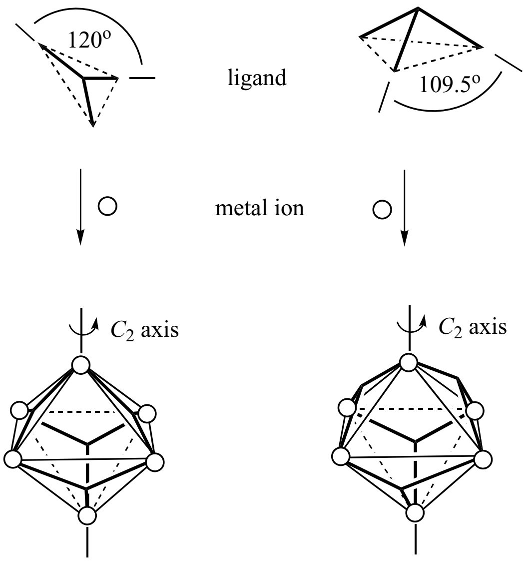
	Corners occupied	Edges occupied	Faces occupied	Assembly descriptors
tetrahedron	4a	6d	–	$A^{3a}_{4}L^{2d}_{6}$
	4d	6a	–	$L^{2a}_{6}A^{3d}_{4}$
	–	6a	4d	$L^{2a}_{6}A^{3d}_{4}$
	–	6d	4a	$A^{3a}_{4}L^{2d}_{6}$
	–	2a/d	2d/a	$A^{4a}_{2}A^{4d}_{2}$, $A^{2a}_{2}A^{2d}_{2}$
	4a	–	4d	$A^{3a}_{4}A^{3d}_{4}$
	4d	–	4a	$A^{3a}_{4}A^{3d}_{4}$
	1a/d	–	1d/a	$A^{3a}_{1}A^{3d}_{1}$
	2a & 2d	–	–	$A^{3a}_{2}A^{3d}_{2}$
	–	2a & 4d	–	$A^{4a}_{2}L^{2d}_{4}$, $A^{4a}_{2}A^{2d}_{4}$, $L^{4a}_{2}A^{2d}_{4}$
	–	4a & 2d	–	$A^{2a}_{4}L^{4d}_{2}$, $A^{2a}_{4}A^{4d}_{2}$, $L^{2a}_{4}A^{4d}_{2}$
	–	1a & 1d	–	$A^{2a}_{1}A^{2d}_{1}$
	–	–	2a & 2d	$A^{4a}_{2}A^{4d}_{2}$, $A^{2a}_{2}A^{2d}_{2}$
		self-cyclized		A^{2a1d}_{4}, A^{1A2d}_{4}, A^{2a2d}_{2}
cube	8a	12d	–	$A^{3a}_{8}L^{2d}_{12}$
	8d	12a	–	$L^{2a}_{12}A^{3d}_{8}$
	–	12a	6d	$A^{2a}_{12}A^{4d}_{6}$
	–	12d	6a	$A^{4a}_{6}A^{2d}_{12}$
	8a	–	6d	$A^{3a}_{8}A^{4d}_{6}$
	6a	–	8d	$A^{4a}_{6}A^{3d}_{8}$
	4a/d	–	6d/a	$A^{3a}_{4}A^{2d}_{6}$
	4a/d	–	4d/a	$A^{4a}_{4}A^{4d}_{4}$
	–	4a	2d	$L^{2a}_{4}A^{4d}_{2}$
	–	4d	2a	$A^{4a}_{2}L^{2d}_{4}$
	–	4a/d	4d/a	$A^{2a}_{4}L^{2d}_{4}$, $L^{2a}_{4}A^{2d}_{4}$
	4a & 4d	–	–	$A^{3a}_{4}A^{3d}_{4}$
	2a & 2d	–	–	$A^{5a}_{2}A^{5d}_{2}$
	–	8a/d & 4d/a	–	$A^{2a}_{8}A^{4d}_{4}$, $A^{4a}_{4}A^{2d}_{8}$
	–	4a & 4d	–	$A^{2a}_{4}A^{2d}_{4}$
	–	2a & 2d	-	$A^{4a}_{2}A^{4d}_{2}$
	–	–	4a/d & 2d/a	$A^{2a}_{4}A^{4d}_{2}$, $A^{4a}_{2}A^{2d}_{4}$
	–	–	2a & 2d	$A^{4a}_{2}A^{4d}_{2}$, $A^{2a}_{2}A^{2d}_{2}$
	–	–	1a & 1d	$A^{4a}_{1}A^{4d}_{1}$
		self-cyclized		A^{2a2d}_{12}, A^{2a2d}_{6}, A^{1a1d}_{4}, A^{2a2d}_{2}, A^{1a1d}_{2}

A much larger number of permutations are available for each of the polygons and polyhedra in Table 2 and Table 3 if three or more building blocks or unsymmetrical building blocks can be used, or if an unsymmetrical overall structure is acceptable.

A systematic analysis of this type reveals the greatest number of design possibilities for the formation of a particular molecular architecture. As such, it enlarges the variety of ligands and metals which can potentially be used. Improvements in the control of the self-assembly process may thereby be realized.

Identifying commonalities between different self-assembly processes: Another use of the classification system is as a means of revealing commonalities between different self-assembly pathways. Three types of commonality may be observed: 1) an identical self-assembly process, 2) a near-identical self-assembly, and 3) self-assembly involving a common building block type. Examples of 1)–3) illustrating their usefulness are given below:

1) Identical self-assembly processes: If one were wishing to prepare a new polyhedron using a particular self-assembly pathway, then a comparison of its assembly descriptor with those in Table 1 reveals any identical self-assembly process previously employed—even if this had generated products of very different overall architecture. Each example of this process provides a precedent which can, theoretically, be altered to generate the desired product. Typical alterations would involve changes to the directing angles or dimensions of the building blocks so that they conform to the symmetry and geometric requirements of the desired architecture. For example, $A^{2a}_{6}A^{3d}_{4}$ assemblies (Table 1) are known to produce truncated tetrahedral architectures like that illustrated in Figure 3a. However, a change in the directing angle of the ligands from 120° to 109.5° should produce a hexanuclear adamantanoid (Figure 4).[6] A formal example of this architecture has not yet been reported, although a suitable ligand is known.[6b]



$A^{2a}_{6}A^{3d}_{4}$ $A^{2a}_{6}A^{3d}_{4}$

Truncated Tetrahedron Hexanuclear Adamantanoid

Figure 4. Schematic depiction of the formation of a truncated tetrahedron and a hexanuclear adamantanoid.[6] The architectures have different overall structures, but identical modes of self-assembly.

2) Near-identical self-assembly processes: Nonidentical but similar self-assembly processes also offer comparative precedents which can potentially be modified to generate a desired architecture. For example, if one were wishing to prepare the $A^{4a}_{6}A^{3d}_{8}$ octahedron architecture described earlier and depicted in Figure 3c, then a search through Table 1 would reveal this to be a mode of assembly with no identical precedent. However, several near-identical descriptors exist, for example, the descriptor $A^{2a}_{6}A^{3d}_{4}$ for the truncated tetrahedra in Figure 3a. This descriptor involves a metal ion having half the desired topicity with an accompanying reduction in the stoichiometry of the ligand. A good starting point would therefore be to modify a system which normally assembles an $A^{2a}_{6}A^{3d}_{4}$ truncated tetrahedra in such a way that it is capable of generating an $A^{4a}_{6}A^{3d}_{8}$ octahedron. The metal ion in such a system would have to be able to undergo the desired four coordination. Likely modifications could involve the use of labile, weakly bound co-ligands and an appropriate excess of the ligand. If the system shown in Figure 3a were employed, the Pd^{II} ion would ideally be induced to adopt an overall five- or six-coordinate disposition in which four adjacent sites were occupied by the bridging ligands with the remaining sites occupied by strongly coordinated co-ligands.

3) Self-assemblies involving common building blocks: Because each building block is uniquely identified in the descriptor classification, all known building blocks of a particular topicity and type can be readily identified by searching through Table 1. For example, consider Albrecht's recent elucidation of the versatility of tritopic ligands in the formation of molecular polyhedra.[10] All compounds containing such ligands have assembly descriptors which include A^{3d} units. Thus, a search for A^{3d} components in Table 1 would reveal all of the compounds included in Albrecht's work. Similar searches can be carried out for any other acceptor or donor type. A known building block whose geometry is suitable for use in the formation of a novel polyhedron or polygon may thereby be revealed. This use of "old" ligands in "new" polygons/polyhedra has already been informally employed; for example, a diplatinum unit has been used in the formation of square,[11] hexagon,[12] and dodecahedron[13] architectures. Other examples can be readily envisioned.

Identifying "switchable" polygons and polyhedra: The concept of "molecular machines" has led to increasing interest in molecular systems which can be made to switch reversibly from one state to another. This has also manifested itself in the field of molecular polyhedra and polygons, with a recent report describing switching between a triple helicate and a tetrahedron.[3] The assembly descriptor classification is well-suited to the systematic identification of switchable polygons and polyhedra. For example, a quick survey of Table 3 reveals identical stoichiometry and building block topicity for the first descriptor listed for each of the tetrahedron ($A^{3a}_{4}L^{2d}_{6}$) and the cube ($A^{3a}_{8}L^{2d}_{12}$). Thus, a change in the directing angles of the acceptor units in an $A^{3a}_{4}L^{2d}_{6}$ tetrahedron from 109.5° (tetrahedral) to 90° (square planar) could lead to its spontaneous conversion to an $A^{3a}_{8}L^{2d}_{12}$ cube (and vice versa). In unrelated systems, electrochemical switching of a similar type has been achieved using a Cu^{I}/Cu^{II} couple.[14]

Conclusion

Atwood and MacGillivray have described in great detail the many different possible spheroidal shapes that synthetic containers may adopt.[5] Stang and Raymond and co-workers[3, 4] have described how to determine the essential geometric and symmetry relationships necessary for the generation of such structures. We have in this work further formalized this general approach by focusing on the self-assembly processes available. A classification system has been developed to uniquely describe combinations of metals and ligands suitable for the formation of particular structures. The new descriptors allow a systematic retrosynthetic analysis of acceptor–donor combinations. They widen the variety of design possibilities available and thereby offer greater control of the self-assembly process. They also permit a ready comparison with previous self-assembly processes of similar stoichiometry and type. By revealing useful commonalities and relationships, they aid in the conceptualization of pathways leading to novel molecular architectures. Finally, they provide a convenient and systematic means of identifying assemblies capable of being switched from one architecture to another.

Taken in concert with the earlier technology in this field, a comprehensive and complementary suite of techniques now exist for the controlled and rational preparation of 2D and 3D molecular containers.

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[1] a) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853–908; b) D. L. Caulder, K. N. Raymond, *Acc. Chem. Res.* **1999**, *32*, 975–982.

[2] Examples of the many possible applications of geometric metallocyclic *polygons* and *polyhedra* are discussed in ref. [1a].

[3] D. L. Caulder, K. N. Raymond, *Dalton Trans.* **1999**, 1185–1200, and references therein.

[4] a) P. J. Stang, B. Olenyuk, *Acc. Chem. Res.* **1997**, *30*, 502–518; b) P. J. Stang, *Chem. Eur. J.* **1998**, *4*, 19–27; c) B. Olenyuk, A. Fechtenkötter, P. J. Stang, *J. Chem. Soc. Dalton Trans.* **1998**, 1707–1728.

[5] L. R. MacGillivray, J. L. Atwood, *Angew. Chem.* **1999**, *111*, 1080–1096; *Angew. Chem. Int. Ed.* **1999**, *38*, 1019–1033.

[6] The structural motif of a truncated tetrahedron is described in: a) S. Leininger, J. Fan, M. Schmitz, P. J. Stang, *Proc. Natl. Acad. Sci. USA* **2000**, *97*, 1380–1384. The formal distinction between a *truncated tetrahedron* and a *hexanuclear adamantanoid* is illustrated on p. 857 in ref. [1a] these two motif types differ only in the directing angle of the ligands (109.5° in an adamantanoid but 120° in a truncated tetrahedron). A "super-adamantanoid" involving a ligand which is theoretically capable of forming a strict adamantanoid has been reported in: b) S. L. James, D. L. P. Mingos, A. J. P. White, D. J. Williams *Chem. Commun.* **1998**, 2323–2324.

[7] D. W. Johnson, J. Xu, R. W. Saalfrank, K. N. Raymond, *Angew. Chem.* **1999**, *111*, 3058–3061; *Angew. Chem. Int. Ed.* **1999**, *38*, 2882–2885.

[8] An example of an octahedron in which all of the faces are occupied by ligands has not yet been reported.

[9] G. F. Swiegers, T. J. Malefetse, *Chem. Rev.* **2000**, *100*, 3483–3537.

[10] M. Albrecht, *Angew. Chem.* **1999**, *111*, 3671–3674; *Angew. Chem. Int. Ed.* **1999**, *38*, 3463–3465.

[11] P. J. Stang, N. E. Persky, J. Manna, *J. Am. Chem. Soc.* **1997**, *119*, 4777–4778.

[12] J. Manna, C. J. Kuehl, J. A. Whitford, P. J. Stang, D. C. Muddiman, C. D. Hofstadler, R. D. Smith, *J. Am. Chem. Soc.* **1997**, *119*, 11611–11619.

[13] B. Olenyuk, M. D. Levin, J. A. Whiteford, J. E. Shield, P. J. Stang, *J. Am. Chem. Soc.* **1999**, *121*, 10434–10435.

[14] For example: J.-P. Collin, P. Gaviña, J.-P. Sauvage, *Chem. Commun.* **1996**, 2005–2006.

[15] C. A. Hunter, R. K. Hyde, *Angew. Chem.* **1996**, *108*, 2064–2067; *Angew. Chem. Int. Ed. Engl.* **1996**, *36*, 1936–1939.

[16] a) M. Fujita, O. Sasaki, T. Mitsuhashi, T. Fujita, J. Yakazi, K. Yamaguchi, K. Ogura, *Chem. Commun.* **1996**, 1535–1536; b) M. Fujita, J. Yakazi, K. Ogura, *J. Am. Chem. Soc.* **1990**, *112*, 5645–5647.

[17] T. Beissel, R. E. Powers, K. N. Raymond, *Angew. Chem.* **1996**, *108*, 1166–1168; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1084–1086.

[18] S. Mann, G. Huttner, L. Zsolnai, K. Heinze, *Angew. Chem.* **1996**, *108*, 2983–2984; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*,2808–2809.

[19] C. Brückner, R. E. Powers, K. N. Raymond, *Angew. Chem.* **1998**, *110*, 1937–1940; *Angew. Chem. Int. Ed.* **1998**, *37*, 1837–1839.

[20] M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi, K. Ogura, *Nature* **1995**, *378*, 469–471.

[21] G. F. Swiegers, T. J. Malefetse, *Coord. Chem. Rev.*, in press.

0947-6539/01/0717-3643 $ 17.50+.50/0