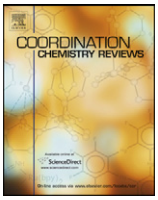
Coordination Chemistry Reviews 255 (2011) 2104–2110

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Ligand design for hollow spherical complexes

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Contents

ARTICLE INFO

Article history:
Received 9 December 2010
Accepted 23 March 2011
Available online 29 April 2011

Keywords:
Molecular cages
Self-assembly
Cyclopentadienyl
Polyhedral
Complexes

ABSTRACT

Coordination chemistry may be used to synthesise large molecules with a closed cavity of molecular dimensions and of roughly equal size in three dimensions. The systems discussed here will involve polytopic ligands linked into spherical shapes by metal coordination. After discussing general strategies for their synthesis using the coordinate bond, studies on systems possessing five-fold symmetry are discussed. This is particularly favourable for the formation of spherical molecules, and some of the problems of multicomponent self-assembly are discussed. After reviewing some recent work, it is suggested that either the combination of three-fold symmetry with four-fold or five-fold symmetry is particularly suitable for sphere formation.

1. Introduction

A truly spherical molecule cannot be constructed with a finite number of atoms. For the purpose of this review we shall consider spherical molecules to be those with their component parts, atoms or molecules, distributed in a regular manner over the surface of a hypothetical sphere, forming a closed, convex and hollow molecule. Fullerene, C_{60}, is of course the obvious example of such a molecule. These systems represent a considerable synthetic challenge but offer several interesting properties, such as microencapsulation of reagents, or as spatially limited reaction vessels. The groups of Fujita and co-workers [1,2] and Raymond and co-workers [3,4] have already reported on the remarkable differences in reactivity observed inside such microflasks. Biological systems have of course developed a large number of routes to synthesising closed compartments [5]. For chemists to use such systems reliable synthetic methods will need to be developed. It is the purpose of this review to discuss synthetic methods using the coordinate bond, and in particular the approach we have been using in recent years. We will concentrate on systems, which may be described as $(\text{ligand})_m(\text{linker})_n$ where "ligand" represents an organic molecule with several coordination sites, and "linker" is a metal containing species, which coordinates to the ligand, and will discuss the design of ligands, which favour the formation of spherical complexes.

2. Synthetic strategies

The obvious route to making a sphere might seem to be the joining of two hemispheres; this was indeed the method first used by Cram et al. [6] to create the carcerands, covalently linking two hemispherical resorcarenes. A high dilution method was used to avoid oligomerisation, since four bonds are formed across the rims of the two hemispheres. Rebek and co-workers [7] used a slightly different approach: although two half units were used, they were

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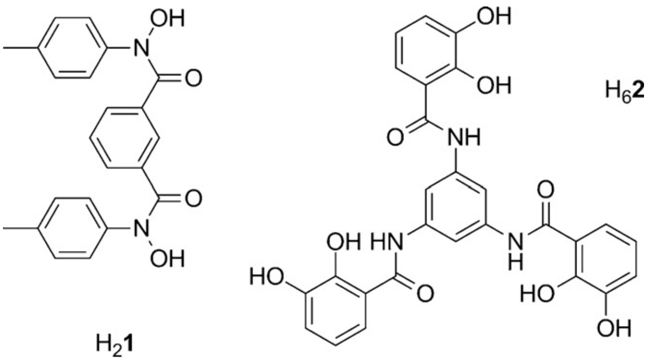
doi:10.1016/j.ccr.2011.03.021



Scheme 1. Ligands **1** and **2**.

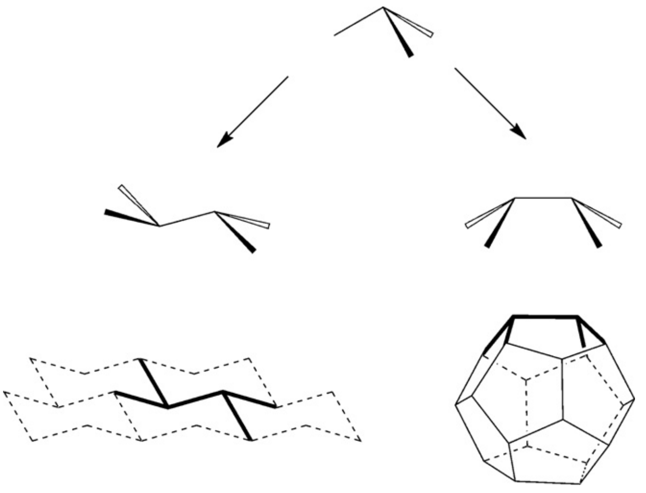
no longer hemispheres but may be best described as the curved surfaces separated by the grooves of a tennis ball. The two units self-assembled by suitably positioned hydrogen bonds. These two examples illustrate nicely two of the problems associated with sphere synthesis: firstly the closing of the molecule requires formation of at least two bonds (and normally more) in contrast to macrocyclic chemistry where a single bond suffices, and secondly, if a small number of components is used, curvature must be present in the components. The use of templates to produce the cyclisation, so effective in macrocyclic chemistry, is generally limited by the difficulty of extracting the template from the closed molecule.

Self-assembly reactions, using predictable and reversible interactions, have established themselves as highly effective routes for the synthesis of large molecules where many bonds need to be formed simultaneously [8]. The two favoured interactions are the hydrogen bond, as used by Rebek, and the coordinate bond, and in the remainder of this article we shall concentrate on the coordination approach.

The problem of curvature may be avoided by forming polyhedral structures. The vertices of Platonic polyhedra (the tetrahedron, cube, octahedron, dodecahedron and icosahedron) are equidistant from the centre of gravity and so lie on the surface of a sphere. As the number of faces increases, the structure becomes a closer approximation to a sphere. The faces of a polyhedron are planar and the edges are linear so that there is no necessity to introduce curvature. Thus a self-assembled polyhedron will be a more or less good approximation to a spherical structure. The Platonic and Archimedean polyhedra have symmetry which results in the three dimensions being equal and are thus isometric. The most common approach is to use a metal atom as the vertex of the polyhedron with ligands linking two or more vertices. The ligand may act either as an edge or as a face of the polyhedron. Thus Raymond has prepared tetrahedral cages of formula M_4L_6 with ligand **1** bridging two metals and acting as an edge [9], as well as tetrahedra of formula M_4L_4 with ligand **2** bridging three metals and acting as a face of the tetrahedron [10] (Scheme 1).

The polyhedral approach has proved very successful. Formally a structure built of edges and vertices is a framework, and has open faces. However, the molecular edges have a finite size, which is often large enough to leave only very small holes in the faces in between the edges, giving an essentially closed structure. MacGillivray and Atwood [11] have discussed the use of Platonic and Archimedean polyhedra as well as prisms and antiprisms in the synthesis of spherical molecules. O'Keefe has published a more recent survey of polyhedral structures formed by complexation reactions [12].

The choice of a suitable vertex does not guarantee that a polyhedron will be formed. Consider the pyramidal vertex shown in Scheme 2. It may be linked to another in two ways, the two elements being related by a centre of inversion or a mirror plane.



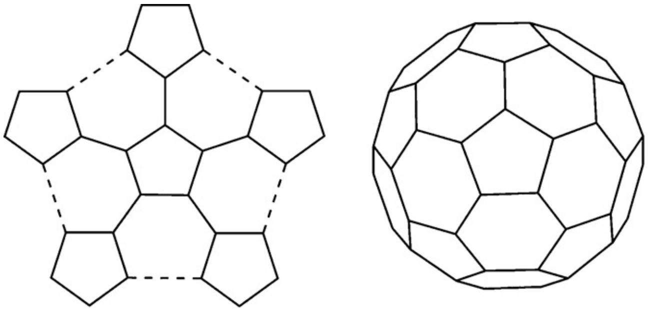
Scheme 2. Pyramidal vertices can combine to give either an extended structure similar to arsenic (left) or a closed, dodecahedral structure (right).

The resulting units can give rise either to an infinite structure such as metallic arsenic, or a closed dodecahedron. Such a dodecahedron has indeed been reported by Stang and co-workers [13] using tris(4-pyridyl)methanol as a vertex linked by a linear diplatinum complex. Clearly there is no obvious preference for the sheet or the closed structure, and indeed both are two-dimensional objects, one in Cartesian coordinates, and the other in spherical coordinates. Another example is the use of the sp^2 carbon atom to generate either the planar structure of graphite or the closed structure of C_{60}. In such systems the two structures will be in competition, and for carbon the balance is strongly in favour of graphite as reflected in the difference by a factor of one million in the price per gram. Consequently, we should seek to incorporate in our ligand features, which favour closed three-dimensional structures over extended two-dimensional ones.

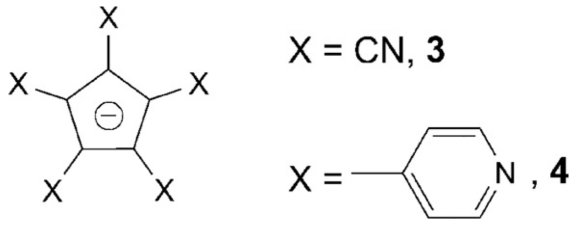
3. The magic pentagon

It is well known that the curvature of fullerenes is related to the presence of the pentagonal cycles in the structures. It is a simple result of crystallography that an extended structure with five-fold symmetry is impossible. Scheme 3 shows what happens when we try to link pentagons by their vertices. For the bonds shown as dashed lines between the outer pentagons to be the same length as those to the central pentagon, the structure must be curved downwards, thus generating a bowl-shaped structure which can propagate by adding further pentagons, finally generating the fullerene structure.

There are now many systems with closed cages showing the symmetry of fullerenes, including, metal–metal bound systems,



Scheme 3. Linking pentagons by bonds of equal length leads to closure and formation of the fullerene structure.



Scheme 4. Ligands **3** and **4**.

polyoxometallates, and coordination compounds [14]. Biology has used pentagonal systems for a long time. In their review of the structure of viruses, Caspar and Klug [5] point out that an icosahedral symmetry offers an efficient way to generate roughly spherical isometric capsules. Muller and co-workers [15–17] have observed the formation of giant cages, the Keplerates, containing pentagonal mixed valence $\mathrm{Mo(Mo)_5}$ oxide units linked by $\mathrm{Mo_2}$ edge-sharing octahedra, and have shown them to have a very rich chemistry. In 2003 Scheer and co-workers [18] reported that the complex $\mathrm{Cp^{*}Fe(P_5)}$ could be linked by copper(I) ions to form a hemisphere which dimerised by coordination to further copper ions to give an almost spherical cavity which did not have the full symmetry of fullerene. They later showed that a more symmetrical species could be formed by using an icosahedral carborane as a template [19]. In both these systems the $\mathrm{P_5}$ ring functions as pentagonal node. They equally found that in many cases a one- or two-dimensional polymer was formed in preference to the closed species [20].

The starting point for our work was the idea that it should be possible to generate a spherical structure using the coordinate bond to link the vertices of pentagonal elements. Such an approach cannot lead to an extended network. In theory the pentagonal vertex could be either a ligand or a metal, but in practice we could think of no metal showing reliable pentagonal coordination and so the choice of a pentagonal ligand was made. The obvious pentagonal unit was the cyclopentadienyl unit, and so our first choices for such ligands were **3** or **4** (Scheme 4).

3.1. *Pentacyanide systems*

Ligand **3** had been prepared many years ago by Webster [21], and has more recently been studied by Richardson and Reed [22] (Fig. 1). The nitrile functionalities of **3** are known to be good ligands for ions such as Ag(I) and Cu(I) which often show linear coordination. The combination of **3** with Ag(I) seemed therefore a good starting point and this was supported by the molecular mechanics simulation of the structure of $[\mathrm{Ag_{30}}(\mathbf{3})_{12}]^{18+}$ which miminised easily to the expected closed symmetrical structure (Fig. 2a). Unfortunately the experiment gave an insoluble brown precipitate analysing as Ag(**3**). Since the structure of **3** is known from the literature, a description of the structure requires only the position of Ag and the position and orientation of the anion **3**. These parameters could be obtained by X-ray powder diffraction, and showed the formation of a chain polymer (Fig. 2b) [23].

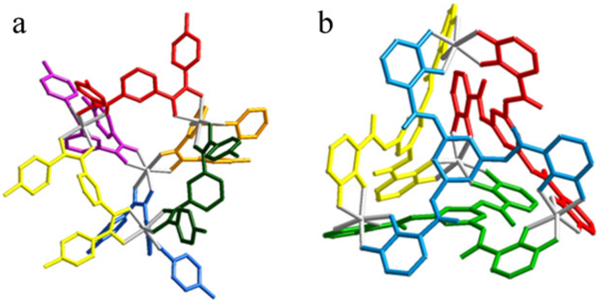


Fig. 1. (a) The structure of the cage $[\mathrm{Ga_4}(\mathbf{1})_6]$ with six edge-bridging ligands [9]; (b)The structure of the cage $[\mathrm{Ti_4}(\mathbf{2})_4]^{8-}$ with four face-bridging ligands [10].

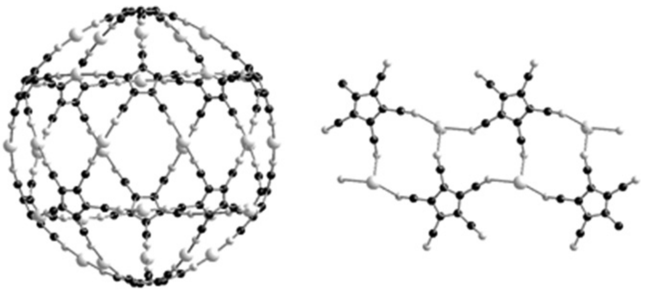


Fig. 2. Theory and practice in spheroid chemistry: (a) The modelled structure of $[\mathrm{Ag_{30}}(\mathbf{3})_{12}]^{18+}$; (b) The observed structure of Ag(**3**).

The result was disappointing, but instructive. One of supramolecular coordination chemistry's favourite principles, that of maximum site occupancy is not respected, with two nitrile functions unused. The ligand does not act as a pentagonal node, and prefers to form a neutral, extended species. The reaction

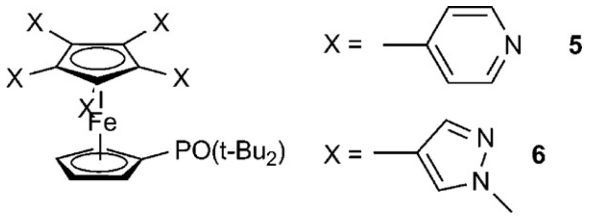
$$12\mathrm{Ag}(\mathbf{3}) + 18\mathrm{Ag}^{+} \rightarrow [\mathrm{Ag_{30}}(\mathbf{3})_{12}]^{18+}$$

is clearly not favourable. The large radius (around 10 Å) of the spheroid will lead to a low solvation energy in spite of the high charge, and may not compensate the lattice energy of the polymer and the loss of solvation of free $\mathrm{Ag^+}$.

3.2. *Pentapyridine systems*

We therefore turned our attention to ligand **4** in the hope that the more strongly coordinating pyridyl ligand would respect the principle of maximum site occupancy. Although ligand **4** could be synthesised [24], it is extremely sensitive to aerial oxidation. This problem could be solved by withdrawing electrons from the Cp ring by binding it to a metal. We prepared ligand **5** by palladium catalysed coupling of 4-bromopyridine to 1-di(t-butyl)phosphinoferrocene using a protocol developed by Hartwig and co-workers [25] to afford the pentasubstituted product. To avoid competition with the pyridyl units in complexation reactions, the phosphine was converted to the phosphine oxide after the coupling (Scheme 5) [24].

Ligand **5** was characterised by X-ray crystallography and showed the five pyridyl units arranged in a pentagonal motif. The complexation of **5** was studied with Cu(I) and Ag(I). ^{1}H NMR spectroscopy showed clearly that **5** bound the metal ions, and an end point was observed at 2.5 equivalents of metal per ligand, as expected for the complex $[\mathrm{M_{30}}(\mathbf{5})_{12}]^{30+}$. Unfortunately crystals could not be obtained neither could a mass spectrum, although this is perhaps not entirely surprising for a species with a +30 charge and labile metal ions. Apart from the observed stoichiometry, the formation of a large cluster was supported by dynamic light scattering and by the dramatic fall in the diffusion coefficient of the ligand upon adding the metal cation. Both measurements were consis-



Scheme 5. Ligands **5** and **6**.

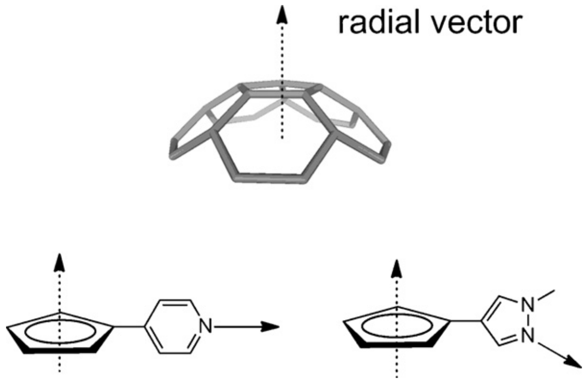


Fig. 3. The pyridyl coordination vector is directed perpendicular to the radial vector whereas the pyrazole coordination vector is slightly inclined. This is closer to the arrangement of the interpentagon bonds in fullerene.

tent with the formation of spherical particles with a radius of 15 Å, which is close to the value calculated by molecular modelling [24].

3.3. Pentapyrazole systems

On the basis of these results, we modified the system in two ways, replacing the pyridyl groups by methylpyrazoles to give ligand **6**, and the linking cation by dirhodiumtetracarboxylates [26]. The first change was to correct for the fact that the pyridyl coordination vector is directed tangentially to the surface of the sphere, while examination of the structure of fullerene suggests that the coordination vector should ideally be directed slightly downwards (Fig. 3). This may be achieved by using a pyrazole.

The use of the dirhodium complex avoids ambiguity concerning the coordination of the linking metal. As we saw above silver(I) may be linear, but can equally be three coordinate. The rhodium carboxylate can only bind bases along the metal–metal bond axis, and must therefore be linear. Incidentally this increases the size of the cluster to give a diameter of 38 Å as estimated from modelling calculations (Fig. 4).

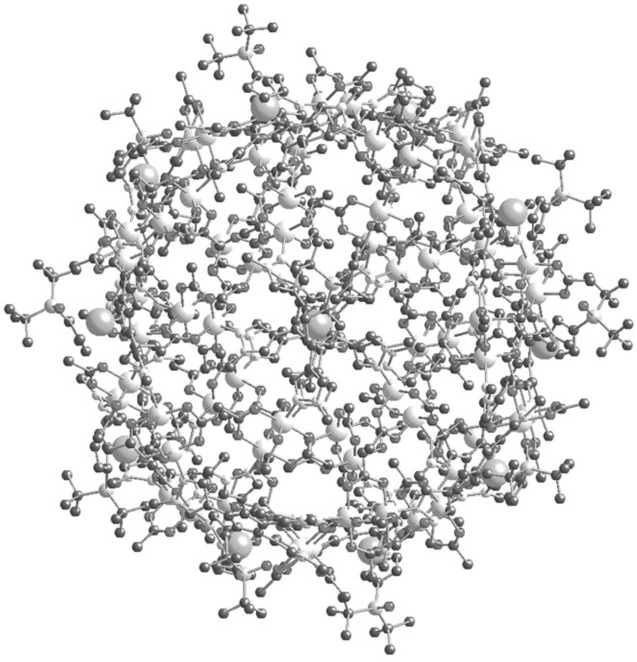


Fig. 4. Modelled structure of $[(\mathbf{6})_{12}\{Rh_2(O_2CH)_4\}_{30}]$.

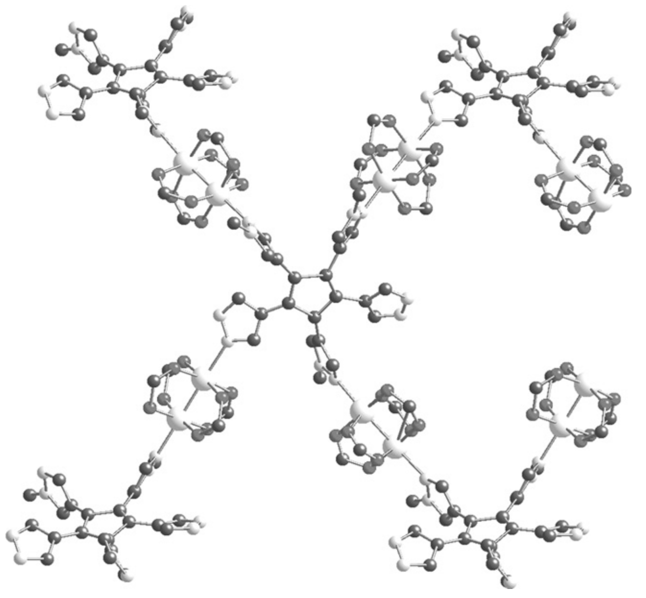


Fig. 5. The network structure of $[(\mathbf{6})\{Rh_2(O_2CC_7H_{15})_4\}_2]$: only the Rh_2 and the pentapyrazolecyclopentadienyl units are shown [26].

The reaction of ligand **6** with $[Rh_2(O_2CC_7H_{15})_4]$ in acetonitrile gives an immediate red precipitate which analyses for $[(\mathbf{6})_{12}\{Rh_2(O_2CC_7H_{15})_4\}_{30}]$. The precipitate dissolves in THF and the ^{1}H NMR spectrum confirms the 2.5:1 metal:ligand ratio, but suggests that rapid exchange takes place. The X-ray powder diagram of the solid can be indexed using a body centred cubic cell with $a = 44.2$ Å. This is consistent with packing of a sphere of diameter 38 Å, close to that obtained from model calculations. Vibrational spectroscopy shows that the dirhodium units are coordinated by two pyrazole ligands. All these data are consistent with the formation of a large sphere, and no other simple explanation seems possible. While the insolubility and absence of crystallinity is disappointing, it is perhaps worth pointing out that the calculated molecular weight of the assembled species is over 30 kDa, larger than many small proteins [26].

On layering the THF solution of $[(\mathbf{6})_{12}\{Rh_2(O_2CC_7H_{15})_4\}_{30}]$ with acetonitrile, red crystals of $[(\mathbf{6})\{Rh_2(O_2CC_7H_{15})_4\}_2]$ are obtained (Fig. 5). In this structure, in a similar way to the pentacyanocomplex, an extended two-dimensional structure is obtained, at the expense of one pyrazole remaining uncoordinated. This raises the interesting question of whether the spherical species is not in fact a kinetic product, the extended sheet forming more slowly [26].

The formation of these fullerene analogues requires the combination of 42 components, and is consequently a relatively complicated self-assembly. The three systems studied here show respectively: a negatively charged ligand with a positive cation, giving rise to a neutral non-spherical polymeric species; a neutral ligand with a positive cation giving a highly charged sphere which remains in solution; a neutral ligand with a neutral but Lewis acidic metal complex which forms a neutral, insoluble sphere. In two cases the rule of maximum site occupancy is broken to allow the formation of a two-dimensional polymeric species.

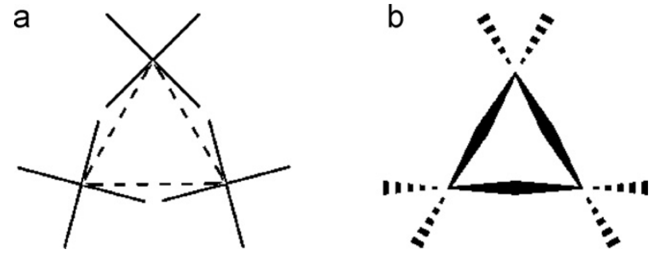
4. Other symmetries for sphere formation

Are pentagons the only route to closed systems? In Scheme 3 we explained the curvature of the assembly of pentagons by the chemically reasonable need to make the bonds linking the vertices of the pentagons the same length. We may look at this in a slightly different way: the equalization of the bond lengths generates a three-fold rotation axis relating three pentagons. This axis is inclined to the five-fold symmetry axis, and it is the successive operations of the inclined symmetry axes that generate the closed structure. We may ask if other combinations of symmetry elements can do the same. Biology has shown that this is indeed possible in the protein ferritin, used to store iron as a FeOOH particle. Ferritin is composed of 24 protein subunits, which may be visualized as bundles of helices [27]. One end of the subunit combines with two other subunits around a three-fold axis while the other end combines with three others around a four-fold axis. The complete structure has 432 symmetry, and forms a hollow ball. The four-fold axis acting on the three-fold axis generates two more three-fold axes, which in turn generate more four-fold axes, leading to closure, just as was seen for the pentagon system. As Raymond has remarked [28], ‘the presence of these two incommensurate *n*-fold symmetry axes can only be achieved by formation of a cluster with octahedral symmetry’.

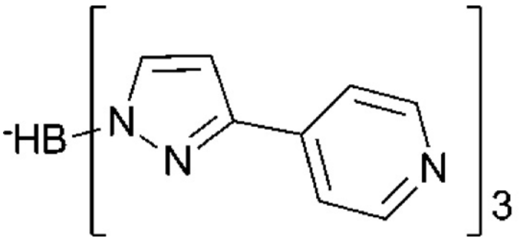
Let us consider combining a four-fold symmetric node such as a square-planar Pd^{2+} ion around a three-fold axis, as shown in Scheme 6. If the linker is linear, then the bond angle of 90° at palladium does not match the 60° required by the three-fold axis if all bonds lie in the plane (Scheme 6a). If the plane of coordination is tilted with respect to the three-fold axis, then the 60° angle is attained, but the four-fold axis is no longer parallel to the three-fold axis. The inclination of the two axes will now lead to curvature. Although it has not generally been recognized, a number of recent publications have reported spheroidal systems containing both three-fold and four-fold axes (Scheme 6).

The first example comes from the group of Batten and co-workers [29,30], where a scorpionate ligand **7** has a 4-pyridyl group grafted on it (Scheme 7). **7** reacts with copper(I) to give a complex with trigonal symmetry with the three pyridyl groups available for complexation. This then reacts with a square planar metal such as copper(II) or an octahedral metal with two coordination sites occupied to give a closed molecule. The second metal provides the four-fold symmetry axis, and leads to a high symmetry caged molecule (Fig. 6).

An intriguing series of complexes has been reported by Fujita and co-workers [31] using palladium(II) with ligands **8** and **9** (Scheme 8). In each case the palladium ion acts as a planar four-coordinate node, with the dipyridyl ligands bridging between them. With ligand **8** a complex $[Pd_{12}(\mathbf{8})_{24}]^{24+}$ is found, whereas ligand **9** gives the complex $[Pd_{24}(\mathbf{9})_{48}]^{48+}$. The structures of the complexes are a cuboctahedron [32] and a rhombicuboctahedron, respectively. Fig. 7 shows the positions of the palladium atoms in these structures.



Scheme 6. Three square-planar node cannot join and respect the angle constraints (a) unless the planes are inclined with respect to the three-fold axis (b).



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Scheme 7. Ligand **7**.

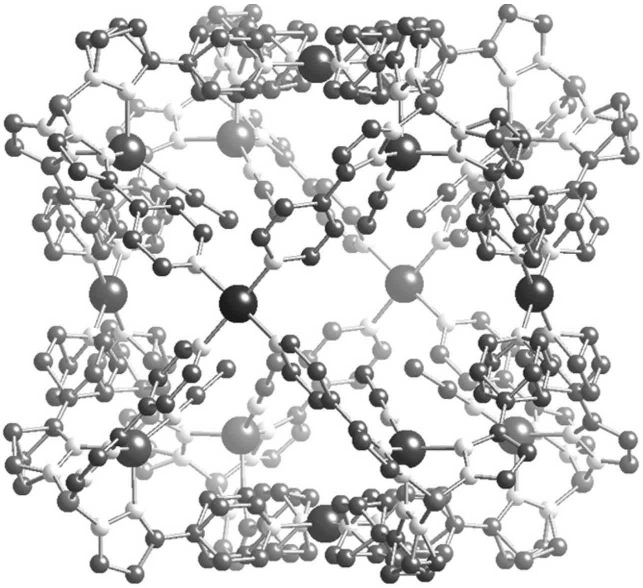
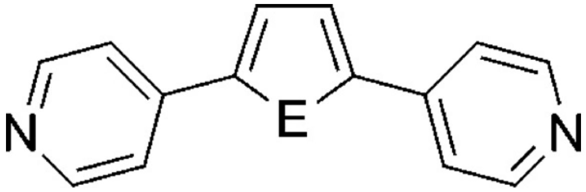


Fig. 6. Structure of the complex $[(\mathbf{7}Cu(I))_8Cu(II)_6]^{12+}$ of Batten and co-workers [29,30] where three-fold symmetric (**7**Cu(I)) units at the corners of a cube are held together by four-fold symmetric square planar Cu(II) ions at the centres of the faces.



E = O, **8**

E = S, **9**

Scheme 8. Ligands **8** and **9**.

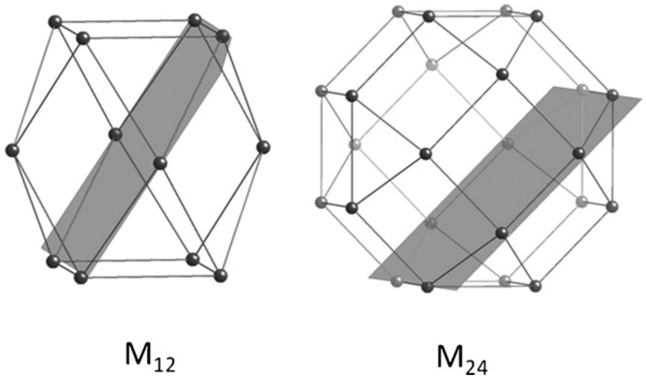
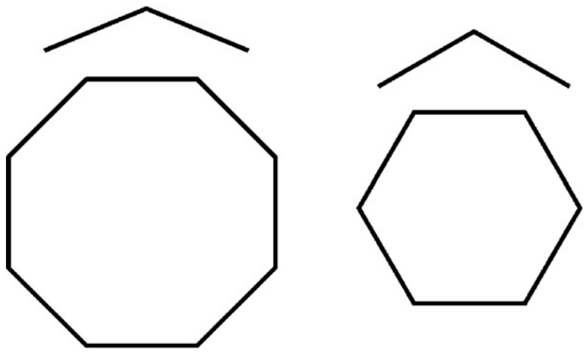


Fig. 7. The positions of the palladium atoms in $[Pd_{12}(\mathbf{8})_{24}]^{24+}$ and $[Pd_{24}(\mathbf{9})_{48}]^{48+}$. The planes show the atoms, which are linked by the planar ligands **8** and **9**.

Both structures show cubic symmetry with incommensurate three-fold and four-fold axes. As the number of vertices increases, the inclination between the square-planar ions at each vertex will decrease. This may be seen simply by considering the two planes



Scheme 9. The angle between the tangents to an octagon is 135°; the corresponding angle for a hexagon is 120°.

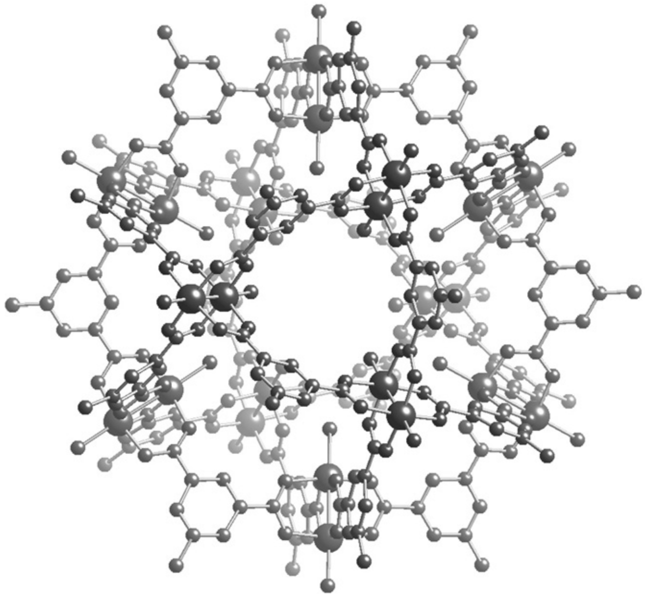


Fig. 8. Structure of $[(Cu_2)_{12}(5\text{-}t\text{-butyl-1,3-benzenedicarboxylate})_{24}]$ redrawn from Ref. [33]. The disordered methyl groups of the *t*-butyl functions have been omitted.

highlighted in Fig. 7, which contain 6 and 8 atoms, respectively. Scheme 9 shows that the angle between tangential lines at two vertices of an octagon is much larger (135°) than that at the vertices of a hexagon (120°). Fujita calculated the angles subtended by the ligands **8** and **9** to be 127° and 149°, respectively. The observed structures thus agree with the relative bond angles (Scheme 9).

A similar effect has been found by the group of Zhou using copper(II) tetracarboxylates [33]. The dicopper unit assembles four carboxylates in a planar four-coordinate motif. In comparison with Fujita's work the dicopper replaces the palladium and the dicarboxylate replaces the dipyridyl unit. With 5-*t*-butyl-1,3-benzenedicarboxylic acid, which has a 120° angle between the carboxylate binding vectors he observes a cuboctahedral structure (Fig. 8). He has studied the effects of ligand exchange on these structures. He has recently extended this work to dimolybdenum tetracarboxylates [34].

In the examples discussed above, the metal generates the four-fold symmetry axis, but it can also arise from the ligand. Atwood has developed an elegant chemistry using resorcin[4]arenes and pyrogallol[4]arenes with four-fold symmetry, which can be linked by hydrogen bonds [35] or by metal ion coordination [36,37] to give large, highly symmetric hollow capsules. In an example with a three-fold symmetric ligand a cyclotriveratrylene ligand has been combined with the square planar palladium(II) ion to give a stella octangular structure [38]. In both these cases the ligands possess not only one of the elements of symmetry but also have an inherent curvature, which favours the formation of a closed structure.

5. Concluding remarks

In this brief review of spherical systems held together by coordinate bonds, I hope to have shown that there has been steady growth in recent years. It is interesting to note that the new structures discussed above are all based on the regular polyhedra which MacGillivray and Atwood [11] proposed to use as target structures to enclose space. Recent systems often contain very large numbers of component molecules (the current record is probably Fujita's system with 72 components [31]), have molecular masses comparable with proteins, and dimensions on a scale of nanometres. It is striking that most of the recent systems display symmetry elements, most typically three-fold axes inclined to a four-fold or five-fold axis, which favour the closure of the systems, and this is proposed as a useful synthetic design principle. It has the useful property that the size of the sphere may be modified by changing the size of the relatively simple components while maintaining the symmetry of the assembly.

The characterisation of these very large molecules raises new problems for coordination chemists. The large number of components results in species assembled from charged entities having high final charges; those assembled from neutral species may be very poorly soluble. There are many other questions that remain to be studied: the stability of these multicomponent species and their kinetics: Fujita has shown, for example, that ligand exchange in his $M_{12}L_{24}$ systems can be very slow [39]. Once reliable synthetic methods are established, the problems of filling or emptying the capsules will need to be solved. There are many interesting aspects of this chemistry yet to be discovered.

Acknowledgements

The experimental work described here was carried out over several years by the members of the Geneva football team, in chronological order: Mirka Bergamo, Carlos da Silva, Thibaut Jarosson, Olivier Oms, Lok Tong, Paulina Aguirre and Damien Simond, and I thank them for their hard work and inspiration. This work was supported by the University of Geneva and the Swiss National Science Foundation.

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