Molecules and crystals with both icosahedral and cubic symmetry†‡

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Notwithstanding the apparent incompatibility between octahedral and icosahedral symmetries, fragments with the two types of symmetry coexist in many molecules and crystals, as evidenced by continuous shape and symmetry measures. A geometric analysis of Platonic and Archimedean polyhedra and of a variety of molecular and crystal structures strongly suggests that octahedral symmetry is latent in icosahedral polyhedra and *vice versa*. In this Feature Article, new concepts and structural data from the literature combine to offer a perspective view of complex molecular and extended structures. Its influence on the common cubic packing of icosahedral molecules is discussed for a variety of examples, including water clathrates, dodecahedrane, Buckminsterfullerene, the Pd_{145} and Mo_{132} clusters and several intermetallic phases.

> *Kepler stared, weeping, at the five polyhedra*
> *fit into each other, systematic, perfect,*
> *with musical order up to the great sphere.*
> *He loved the dodecahedron, wept over the icosahedron*
> *for its inconsistencies and intricacies*
> *lovely and odd but, oh!, so necessary,*
> *since one cannot conceive more perfect solids*
> *beyond the five known, in three dimensions.*
>
> Gabriel Celaya

Introduction

The highest degree of symmetry that can be found in a molecule is represented by the icosahedral (I_h) and octahedral (O_h) point groups.[1] While they have some symmetry operations in common, forming the D_{3d} and T_h subgroups (**1**),[2] fivefold rotations are exclusive of the icosahedral and fourfold rotations appear only in the octahedral point group. We are concerned in this work with systems in which a set of atoms of octahedral symmetry is combined with another one of icosahedral symmetry in a composite that has formally T_h

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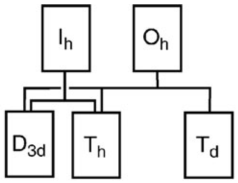
† Dedicated to David Avnir on his 60th birthday.

‡ Electronic supplementary information (ESI) available: Table S1: Shape measures of the M_8 and X_{12} groups relative to the cube and the icosahedron, respectively, in the family of compounds of general formula $[M_8(AX_2)_6]$. Fig. S2: Representation of one plane of the Cs_8Sn_{46} structure showing four of the six edge-sharing Cs_{12} icosahedra connected to the central one that are responsible for a primitive cubic packing. Fig. S3: Perspective view of the nearly perfect cuboctahedral arrangement of the nearest neighbour $(H_2O)_{60}$ clusters that form part of the $(H_2O)_{100}$ nanodrops in the guanidinium salt of a Mo_{132} complex. See DOI: 10.1039/b719615f

symmetry, losing the four- and fivefold operations of the octahedron and the icosahedron, respectively. An interesting finding is that in many chemical systems of this type each component retains all or most of its original higher symmetry in the aggregate.



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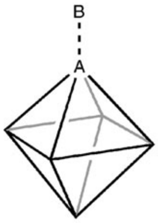

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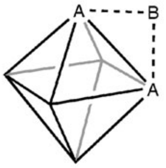

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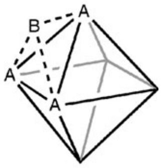

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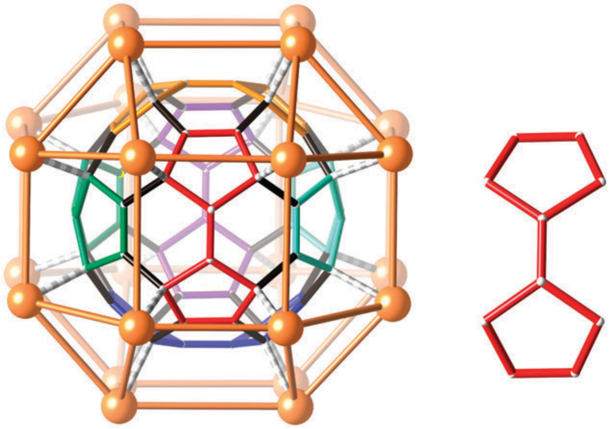

Fig. 1 View of the structure of $C_{60}Br_{24}$ that combines the icosahedral symmetry of the C_{60} fullerene skeleton with a concentric truncated cubic Br_{24} shell (yellow spheres). The fullerene skeleton is depicted as six fulvalene units (right) in different colors, arranged at the vertices of an octahedron and linked through C–C bonds depicted in black. The yellow sticks do not represent chemical bonds and are shown only to highlight the Br_{24} rhombicuboctahedron.

A rather common structural motif in chemistry is a polyhedral set of atoms which often appears circumscribed by one or more concentric polyhedral shells, as in Keplerates.[3] The name Keplerate has been proposed for a group of atoms organized in spherical shells around a central point in such a way that each set of symmetry-related atoms corresponds to the vertices of a Platonic or a generalized Archimedean solid.[4] Two successive shells in those systems are connected—*via* ionic, metallic, covalent or hydrogen bonding—by vertex (**2a**), edge (**2b**) or face (**2c**) capping, as schematically shown in **2**, where the bonding between shells A and B is indicated by dashed lines. The shape of a polyhedron B_m circumscribed around polyhedron A_n is therefore determined by the chemical bonding between the two shells, following precise geometrical rules.[5,6] Furthermore, we usually expect the symmetry of two shells to be the same or to present a group-subgroup relationship, as in the *ligand polyhedral model* proposed by Johnson that considers the nested polyhedra formed by a cluster of metal atoms and its coordinated ligands.[7] For instance, in clusters of the general formula $[M_6(\mu\text{-}X)_8L_6]$, in which the metal atoms form a regular octahedron, the terminal ligands L form also an octahedron and the bridging ligands X a cube, all three polyhedra belong to the O_h symmetry point group. In another example, a Pd_{145} cluster reported by Dahl and co-workers,[8] up to six nested Pd polyhedra can be found, all of them presenting icosahedral symmetry. It has also been shown[9] that a number of Keplerates present concentric polyhedra having all icosahedral symmetry and this constitutes a general *Aufbau* principle. Nevertheless, a variety of molecular structures show that the three symmetries of the Platonic solids (O_h, I_h and T_d) have some hidden relationships that may show up under specific substitution patterns. In particular, we show in this work that the octahedral symmetry is implicit in the icosahedron and the dodecahedron, as well as in Archimedean polyhedra with icosahedral symmetry. Furthermore, we will show that those relationships appear in a variety of molecules and play a crucial role in their packing in the solid state.

Let us consider as a first example the C_{60} fullerene, which has the shape of a truncated icosahedron belonging to the icosahedral symmetry point group I_h. In its halogenated derivatives $C_{60}X_{24}$ (X = Cl, Br), prepared and characterized by Troyanov *et al.*,[10] the halogen atoms are beautifully organized at the vertices of a slightly distorted rhombicuboctahedron (Fig. 1). It is remarkable that by appending Br atoms to a structure with icosahedral symmetry we can generate a concentric shell with approximately octahedral symmetry. Is this a coincidence or a rarity? Or is there some deeper relationship between the two most symmetrical groups? A closer look at the C_{60} structure tells us that it could be described as an octahedral arrangement of six fulvalene units linked through C–C bonds (Fig. 1). Indeed, the centers of such fulvalene units form a perfect octahedron, as revealed by a zero value of its octahedral shape measure,[11] indicating that the octahedral symmetry is latent in a set of edge centers of the truncated icosahedron. The fact that the substituted carbon atoms do not form a square accounts for the deviation of Br_{24} from a perfect rhombicuboctahedron. But that does not rule out the latency of octahedral symmetry in the truncated icosahedron. For instance, Hirsch and co-workers were able to cyclopropanate precisely the six central carbon–carbon bonds of the fulvalene units,[12] and the six additional carbon atoms form a perfect octahedron. Similarly, theoretical calculations on an epoxidized fullerene $C_{60}O_6$ show the six oxygen atoms to form a perfect octahedron,[13] although so far only a singly epoxidized fullerene seems to have been prepared.[14]

Latent octahedral symmetry can be found even in the most simple and perfect icosahedral polyhedra, the dodecahedron and the icosahedron. It suffices to select eight faces of the icosahedron related by symmetry planes and place a point at each of such face centers (partial face augmentation[5]) to obtain a perfect cube (Fig. 2(a)). Given the duality relationship

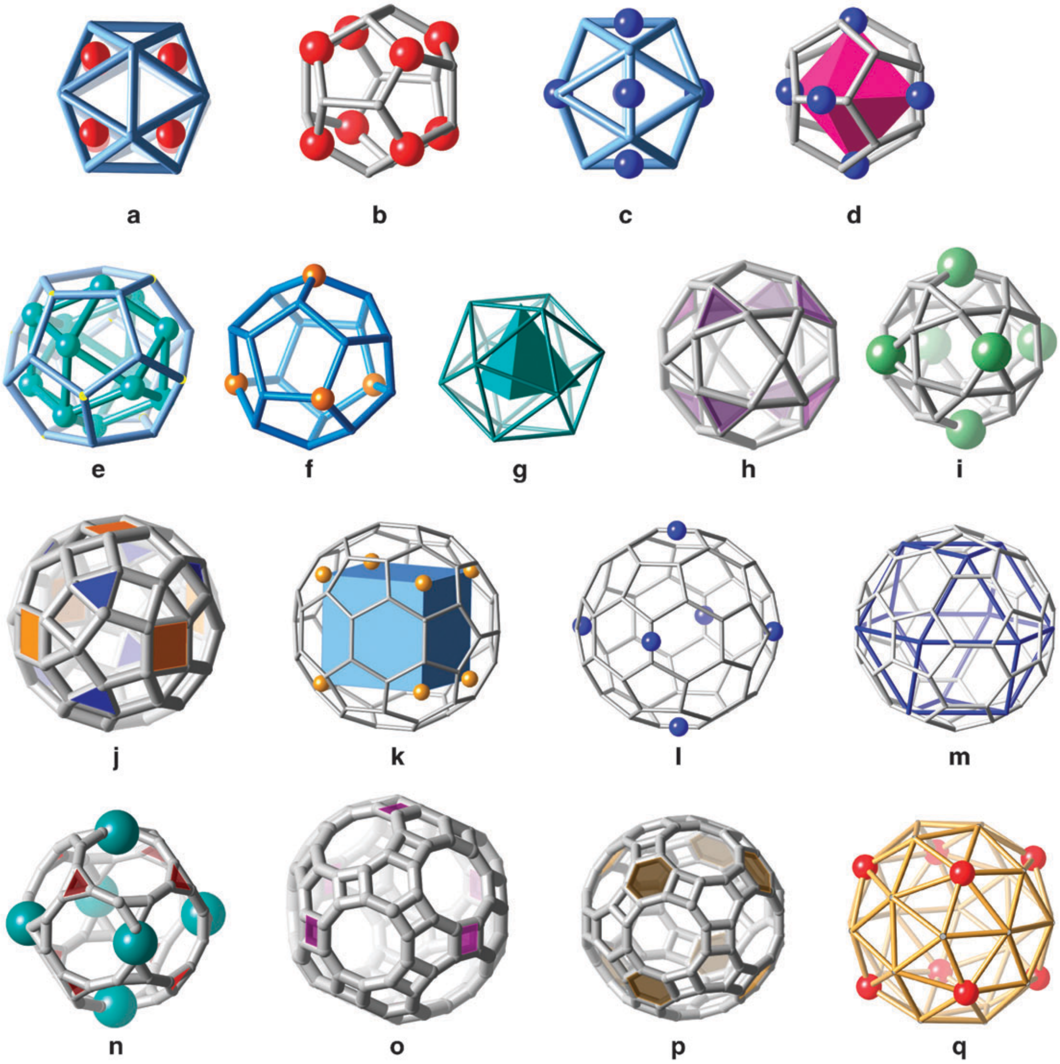

Fig. 2 Polyhedra with octahedral or tetrahedral symmetry implicit in some Platonic, Archimedean and Catalan polyhedra of icosahedral symmetry. (a) Partial face augmentation (spheres) of the icosahedron (sticks) that produces a perfect cube. (b) Subset of eight vertices of the dodecahedron with a perfect cubic shape. (c) Formation of an octahedron (spheres) by augmentation of six edges of the icosahedron (sticks). (d) Build-up of an octahedron (spheres) by augmentation of six edges of the dodecahedron (sticks). (e) Cuboctahedron in a dodecahedron. (d) Tetrahedron in a dodecahedron. (g) Tetrahedron in an icosahedron. (h) Cube (centers of the highlighted triangular faces) in an icosidodecahedron. (i) Octahedron in an icosidodecahedron, (j) cube (centers of highlighted square faces) and octahedron (centers of highlighted triangular faces) in a rhombicosidodecahedron. (k) Cube in a truncated icosahedron. (l) Octahedron in a truncated icosahedron. (m) Cuboctahedron in a truncated icosahedron. (n) Cube (centers of highlighted triangular faces) and octahedron (spheres) in a truncated dodecahedron. (o) Octahedron (centers of highlighted squares) in a truncated icosidodecahedron. (p) Cube (centers of highlighted hexagons) in a truncated icosidodecahedron. (q) Cube in a pentakisdodecahedron.

between the dodecahedron and the icosahedron, that converts one polyhedron into the other one by exchanging vertices by face centers, it is obvious that a cube can also be generated from a dodecahedron by selecting a subset of eight vertices related by orthogonal symmetry planes (Fig. 2(b)). It follows that icosahedral Platonic solids bear also a relationship with the octahedron. Taking advantage of the duality relationship between the cube and the octahedron, we need only replace the six faces of the cubes in Fig. 2(a) and (b) by vertices. It can then be seen that this implies augmentation (capping) of six edges, both for the icosahedron and the dodecahedron (Fig. 2(c) and (d)).

If the cube and the octahedron can be generated from the dodecahedron and the icosahedron, the inverse relationship should also hold. The simplest relationship from the chemical point of view corresponds to the generation of an icosahedron around a cube *via* edge augmentation, *i.e.*, placing twelve atoms above the centers of the twelve edges of the cube. Such a relationship can be appreciated in Fig. 2a. Similarly, cubic polyhedra are imprinted in all the icosahedral Platonic and Archimedean solids, as shown by the examples given in Table 1 and represented in Fig. 2.

The chemical relevance of one such fascinating geometrical construction is exemplified by a family of compounds of the general formula $[M_8(AX_2)_6]$, in which M is a tricoordinated monocation of a metal of the copper group and AX_2 is a doubly bridging ligand (with X = S or Se; A = C, P or an

Table 1 Examples of polyhedra with octahedral or tetrahedral symmetry generated by capping components of icosahedral polyhedra

Family	Icosahedral polyhedron	Capping	Octahedral polyhedron
Platonic	Dodecahedron	8 vertices	Cube
		6 edges	Octahedron
		12 corners[a]	Cuboctahedron
		4 vertices	Tetrahedron
	Icosahedron	8 face centers	Cube
		6 edges	Octahedron
		4 faces	Tetrahedron
Archimedean	Icosidodecahedron	8 triangular faces	Cube
		6 vertices	Octahedron
	Rhombicosidodecahedron	8 triangular faces	Cube
		6 tetragonal faces	Octahedron
	Truncated Icosahedron	8 hexagonal faces	Cube
		6 edges	Octahedron
		6 pentagonal faces + 6 edges	Cuboctahedron
	Truncated dodecahedron	8 triangular faces	Cube
		6 edges	Octahedron
	Truncated Icosidodecahedron	8 hexagonal faces	Cube
		6 tetragonal faces	Octahedron
Catalan	Pentakis dodecahedron	8 vertices	Cube
	Rhombic triacontahedron	8 vertices	Cube
		6 faces	Octahedron

[a] We define a "corner" as the centroid of two vertices of a pentagon in relative positions 1 and 3.

organic C_2 fragment). The eight metal atoms are arranged at the vertices of a cube, whose edges correspond to weak d^{10}–d^{10} bonding interactions (Fig. 3). Since each metal atom is coordinated in a monodentate mode by three independent AX_2 ligands with a planar trigonal geometry, there are eight X_3 triangles corresponding to the metal coordination spheres at the vertices of the cube, in which the interligand $X\cdots X_{\mathrm{inter}}$ distances are related to the M–X bond distances as in eqn (1).

$$X\cdots X_{\mathrm{inter}} = \sqrt{3}(M\cdots X) \qquad (1)$$

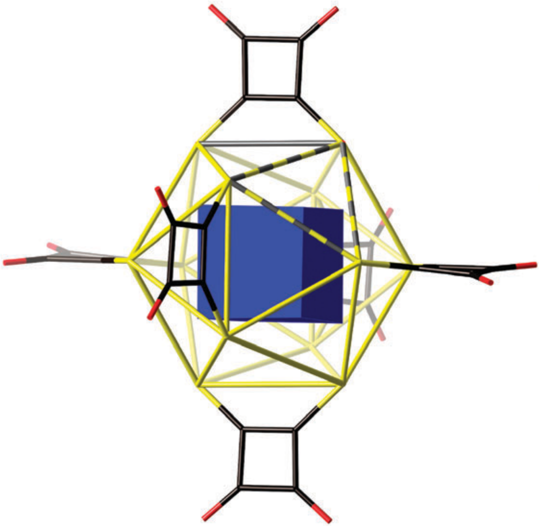

Fig. 3 Icosahedron of sulfur atoms (yellow sticks) circumscribing a cube of Cu atoms in the $[Cu_8(dtsq)_6]^{4-}$ anion. Striped cylinders indicate some of the inter-ligand $X\cdots X'$ edges that form the coordination sphere of a Cu atom, while the gray cylinder corresponds to an intraligand $X\cdots X$ edge.

In addition, there are six $X\cdots X_{\mathrm{intra}}$ intraligand distances within the AX_2 groups, resulting in a total of 30 $X\cdots X_{\mathrm{intra}}$ and $X\cdots X_{\mathrm{inter}}$ edges that form a polyhedron with twenty triangular faces. The only additional requirement for such a polyhedron to be a regular icosahedron is that the intra- and interligand distances $X\cdots X_{\mathrm{intra}}$ and $X\cdots X_{\mathrm{inter}}$ be identical. Therefore, one should expect the $[M_8(AX_2)_6]$ buildings to form nearly perfect X_{12} icosahedra when the choice of metal M, donor atoms X and spacer A is such that the $X\cdots X_{\mathrm{intra}}$ distance obeys eqn (1). Among the family of compounds analyzed (see ESI‡ for data and references), the best example corresponds to the $[Cu_8(dtsq)_6]^{4-}$ anion (dtsq = dithiosquarate, Fig. 3),[15] for which the M_8 set forms a practically perfect cube (cubic shape measure of 0.03) and the X_{12} group has a nearly perfect icosahedral shape (icosahedral shape measure of 0.04). The rest of the compounds found form also very nice cubes and slightly distorted icosahedra. The distortion of the icosahedra is seen to correspond to deviations from eqn (1), since the icosahedral shape measures increase exponentially as the $X\cdots X_{\mathrm{intra}} : \sqrt{3}(M\cdots X)$ ratio deviates from unity (Fig. 4).

Another case of latent symmetry that involves the octahedron can be found in the structure of $[Li_{26}(\mu_6\text{-}O)(ER)_{12}]$ (E = P or As).[16,17] In those molecules we find around a central oxo anion a Li_6 octahedron circumscribed in turn by a Li_{20} dodecahedron (Fig. 5(a)). The vertices of the octahedron are precisely aligned with the centers of edges of the dodecahedron, as discussed above (Fig. 2(d)). In fact, the relationship in such a structure is still more rewarding, since a P_{12} icosahedron appears roughly at the same distance of the central oxygen atom than the Li_{20} dodecahedron (Fig. 5(b)), the two being connected through a duality relationship[5] and composing together a 32-vertex Frank–Kasper polyhedron.[6] The corresponding shape measures for these polyhedra (Table 3, see later) confirm that all of them show a high degree of octahedral and icosahedral symmetry, respectively.

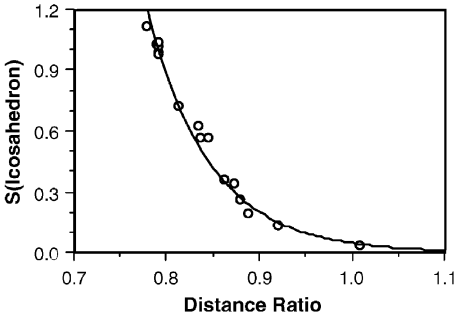

Fig. 4 Dependence of the icosahedral shape measure of the X_{12} set on the $X\cdots X_{intra} : \sqrt{3}(M\cdots X)$ distance ratio in the family of $[M_8(AX_2)_6]$ compounds. The continuous line corresponds to a least-squares fitting to an exponential ($R^2 = 0.990$). The geometrical expectation for a perfect icosahedron and trigonal-planar coordination sphere of the metal atoms corresponds to a ratio of 1 (eqn (1)).

Having seen the latency of the cube in icosahedral polyhedra, it automatically comes to our minds the fact that fullerene and other icosahedral molecules crystallize in cubic space groups, as seen by a few examples shown in Table 2. A naïf interpretation would be that their cubic lattices result from the nearly-spherical nature of these molecules that pack in the same way as the atoms of, *e.g.*, Ni, Cu, Ag, Au, Al or Pb[18] in their elemental structures. However, a careful analysis of intermolecular interactions will show us that the latent cubic symmetry of those icosahedral molecules is in register with their cubic lattices.

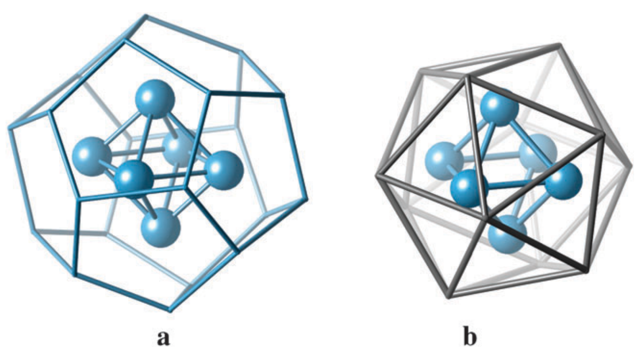

Fig. 5 Partial views of the structure[17] of $[Li_{26}(\mu_6\text{-}O)(PR)_{12}]$ showing (a) the Li_6 octahedron inscribed in a Li_{20} dodecahedron and (b) the same octahedron inscribed in a P_{12} icosahedron.

Let us start by commenting on one of the simplest examples, that of the clathrate I structure present in the hydrates of a variety of small molecules such as CO_2 or methane (Table 2). One way of describing the clathrate I structure focuses on the dodecahedron formed by twelve water molecules, which establishes hydrogen bonds with eight neighbouring dodecahedra through the eight cubic vertices highlighted in Fig. 2(b), therefore resulting in a bcc packing of dodecahedra with space group $Pm\bar{3}n$ (Fig. 6).

A paradigmatic case of cubic crystal structure of an organic compound is that of dodecahedrane ($C_{20}H_{20}$), a long sought for dodecahedral molecule. In the solid state it presents a cubic close packing (fcc),[19,20] in which each molecule is surrounded by twelve nearest neighbours placed at the vertices of a

Table 2 Cubic crystal structures of molecules or clusters with icosahedral symmetry

Compound	Space group	No.	Packing	Cluster	Polyhedron[a]	S(polyhedron)	S(C5)	Ref.
$C_{20}H_{20}$ (dodecahedrane)	$Fm\bar{3}$	202	fcc	C_{20}	Dodecahedron	0.00	0.00	19
				H_{20}	Dodecahedron	0.01	0.01	
C_{60} (fullerene)	$Pa\bar{3}$	205	fcc	C_{60}	Truncated Icosahedron	0.01	0.01	23
						0.01	0.00	21
$C_{60}\cdot H_2C{=}CH_2$	$Pa\bar{3}$	205	fcc	C_{60}	Truncated Icosahedron	0.00	0.00	27
$K_3Ba_3C_{60}$	$Im\bar{3}$	204	bcc	C_{60}	Truncated Icosahedron	0.00	0.00	28
$C_{60}\cdot O_2$	$Fm\bar{3}$	202	fcc	C_{60}	Truncated Icosahedron	0.06	0.06	29
$K_2(B_{12}H_{12})$	$Fm\bar{3}$	202	fcc	B_{12}	Icosahedron	0.01	0.00	30
				H_{12}	Icosahedron	0.00	0.00	
$Cs_2(B_{12}H_{12})$	$Fm\bar{3}$	202	fcc	B_{12}	Icosahedron	0.00	0.00	31
				H_{12}	Icosahedron	0.05	0.05	
Cr_3Si (Cr_3Si type)	$Pm\bar{3}n$	223	bcc	Cr_{12}	Icosahedron	0.81	0.81	32, 51
Cs_8Sn_{46} (K_4Si_{23} type)	$Pm\bar{3}n$	223	bcc	Sn_{20}	Dodecahedron	0.19	0.19	33
			cubic	Cs_{12}	Icosahedron	0.81	0.81	
Na_8Si_{46} (K_4Si_{23} type)	$Pm\bar{3}n$	223	bcc	Si_{20}	Dodecahedron	0.05	0.05	34
			cubic	Na_{12}	Icosahedron	0.81	0.81	
WAl_{12} ($Al_{12}W$ type)	$Im\bar{3}$	204	bcc	WAl_{12}	Icosahedron	0.03	0.03	35
$LaFe_4P_{12}$ ($LaFe_4P_{12}$ type)	$Im\bar{3}$	204	bcc	Fe_8P_{12}	Dodecahedron	0.42	0.42	36
$CaCu_3Ti_4O_{12}$ ($NaMn_7O_{12}$ type)	$Im\bar{3}$	204	bcc	CaO_{12}	Icosahedron	0.05	0.04	37
NaK_9Tl_{13}	$Im\bar{3}$	204	bcc	Tl_{12}	Icosahedron	0.06	0.06	38
$Li_{13}Cu_6Ga_{21}$	$Im\bar{3}$	204	bcc	Ga_{12}	Icosahedron	0.00	0.00	39
				Li_{20}	Dodecahedron	0.00	0.00	
				Cu_{12}	Icosahedron	0.15	0.15	
$Na_{13}(Cd_{1-x}Tl_x)_{27}$	$Im\bar{3}$	204	bcc	$(Cd, Tl)_{12}$	Icosahedron	0.00	0.00	40
				Na_{20}	Dodecahedron	0.00	0.00	
				Cd_{12}	Icosahedron	0.16	0.19	
"Pd_{145}"	$Pa\bar{3}$	205	fcc	Pd_{12}	Icosahedron	0.00	0.00	8
"Mo_{132}"	$Fm\bar{3}$	202	fcc	Mo_{12}	Icosahedron	0.00	0.00	41
$(CO_2)_{7.34}(D_2O)_{46}$	$Pm\bar{3}n$	223	bcc	O_{20}	Dodecahedron	0.04	0.04	42
$(CH_4)_8(H_2O)_{46}$	$Pm\bar{3}n$	223	bcc	O_{20}	Dodecahedron	0.03	0.03	43

[a] Circumscribed polyhedra in the same structure are listed from the innermost to the outermost one.

Table 3 Nearly cubic crystal structures of molecules or clusters with icosahedral or tetrahedral symmetry

Compound	Space group	No.	Cluster	Polyhedron	S(polyhedron)	Packing	S(packing)[a]	S(C_5)	Ref.
$Sm_{2.75}C_{60}$	*Pbca*	61	C_{60}	Truncated Icosahedron	—[b]	fcc	<0.01	—[b]	44
$A_3(B_{12}H_{12})X$[c]	$R\bar{3}m$	166	B_{12}	Icosahedron	≤ 0.001	fcc	0.12–0.19	≤ 0.001	45
B_6O	$R\bar{3}m$	166	B_{12}	Icosahedron	0.18	fcc	0.09	0.15	46
$La_{20}Ni_{30}$	$R\bar{3}$	148	La_{20}	Dodecahedron	0.12	cubic	0.16	0.12	47
$[Li_{26}(\mu_6\text{-}O)(PR)_{12}]$	$P2_1/c$	14	Li_6	Octahedron	0.41	bcc	0.02		16
			P_{12}	Icosahedron	0.04			0.02	
			Li_{20}	Dodecahedron	0.07			0.07	
$[Li_{26}(\mu_6\text{-}O)(AsR)_{12}]$	$P2_1/c$	14	Li_6	Octahedron	0.40	bcc	0.02		17
			As_{12}	Icosahedron	0.05			0.02	
			Li_{20}	Dodecahedron	0.07			0.06	

[a] Shape measure of the nearest neighbours relative to the cuboctahedron (fcc), the cube (bcc) or the octahedron (simple cubic packing). [b] Atomic coordinates of C atoms not available. [c] A = K, Rb, Cs, NH_4; X = Cl, Br.

cuboctahedron. The shortest distances between two neighbouring dodecahedra involve two C–H···H–C contacts (2.40 Å) corresponding to positions 1 and 3 of a pentagon (Fig. 7(a)). In fact, since each vertex belongs to three connected pentagons, each hydrogen atom involved in intermolecular interactions is connected to three different neighbours, forming altogether a tetrahedron of hydrogen bonds (Fig. 7(b)). The outcome, a cuboctahedron (*i.e.*, an fcc packing) of dodecahedra surrounding each particular dodecahedrane molecule, can be seen in Fig. 7(c). In contrast with the capping of the twelve faces of the dodecahedron at their centers, that gives an icosahedron, a set of centroids of atoms in relative positions 1 and 3 of each pentagonal face forms a cuboctahedron, as shown in Fig. 7(d). It was latent in the dodecahedron and it was enough for us to look carefully at the crystal structure of dodecahedrane to recognize its presence. Unsurprisingly, the C_3 symmetry axes and the latent C_4 symmetry axes of the cuboctahedron are coincident with those of the cube that is hidden in the dodecahedron, as discussed above.

Buckminsterfullerene molecules, with their truncated icosahedral shape, also crystallize in an fcc structure, in such a way that each molecule is surrounded by a cuboctahedron of nearest neighbours. The cuboctahedron that defines the nearest neighbour directions is formed by the centers of six pentagonal faces related through an S_6 improper rotation (Fig. 8(a) and (b)) and the centers of six edges shared by two hexagons and related by the same symmetry operation. Such an arrangement of the nearest neighbour directions might suggest that the corresponding intermolecular interactions cannot be equivalent. But the shortest intermolecular contacts (3.175 Å) appear precisely between pentagonal rings and C–C bonds shared by two hexagons[21] (Fig. 8(c)). So each molecule makes ring-edge contacts to six nearest neighbours and edge-ring contacts to six more nearest neighbours.

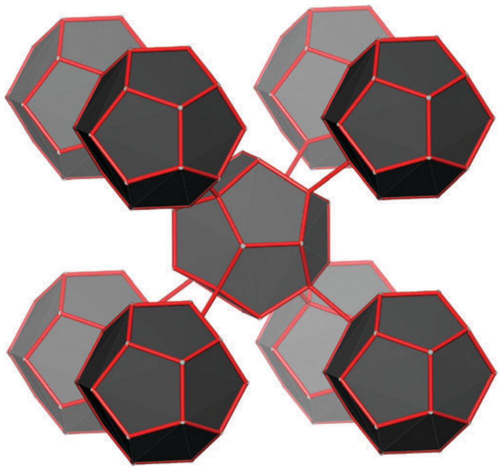

Fig. 6 Cubic packing of dodecahedra of water molecules surrounding CH_4 in the clathrate I structure of the methane hydrate $(CH_4)_8(H_2O)_{46}$.

The octahedral symmetry implicit in icosahedral molecules is probably at the root of the cubic crystal structures found for other types of compounds (Table 2), including boranes, intermetallic phases and polyoxometallates. We notice also that it is not rare to find icosahedral viruses that crystallize in cubic space groups, such as the turnip yellow mosaic virus,[24] the simian virus 40[25] or the polyoma virus.[26] According to the space groups in which they crystallize, we can find cubic close packed (fcc), primitive cubic or body centered cubic (bcc) structures. It must be stressed that some of the compounds analyzed in Table 2 belong to the structural types Cr_3Si, K_4Si_{24}, $Al_{12}W$, $LaFe_4P_{12}$ and $NaMn_7O_{12}$, which comprise altogether well over five hundred structures. For many such structures based on icosahedral polyhedra, the corresponding shape measures tell us that the cubic crystal structure does not prevent individual sets of atoms to be perfect icosahedra, dodecahedra or truncated icosahedra. It is also interesting to analyze those cubic structures in which the icosahedral fragments are distorted to a significant degree, as indicated by S(polyhedron) values larger than 0.1, and compare them with the corresponding C_5 symmetry measures (Table 2). In practically all cases the two measures present the same value, indicating that the distortion of the icosahedral shape is due to the loss of the fivefold rotational symmetry. We have furthermore observed that in those cases at least one trigonal symmetry axis is retained, as indicated by $S(C_3)$ values of 0.00. Such a trigonal distortion in, *e.g.*, the Cs_{12} icosahedral cluster surrounding a $CsSn_{20}$ dodecahedron in Cs_8Sn_{46}, consists in a rotation of six vertices relative to two opposing triangular faces (**3**), thus retaining the corresponding threefold rotational axis while losing the fivefold rotations (T_h symmetry point group). As a result of such a distortion, six edges of the icosahedron are shortened (three of them shown in projection

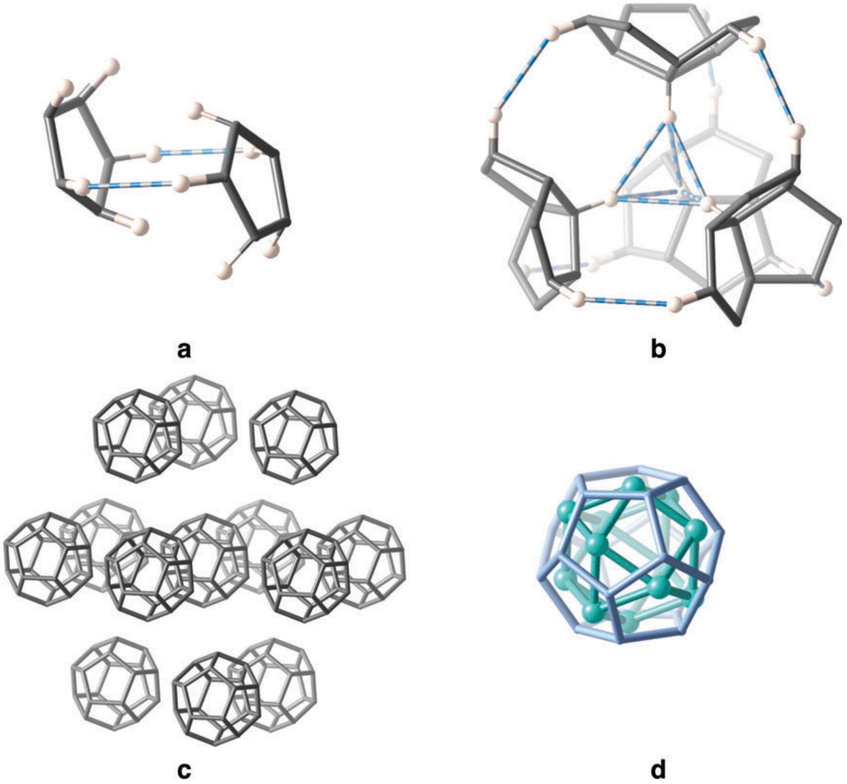

Fig. 7 (a) View of the short C–H···H–C contacts between two neighbouring dodecahedrane molecules in the crystal structure of $C_{20}H_{20}$. (b) Arrangement of four dodecahedrane molecules around a tetrahedron of four connected H atoms (hydrogen atoms not involved in hydrogen bonding between the four molecules partially shown are omitted for clarity). (c) Crystal structure of dodecahedrane showing twelve nearest-neighbour molecules in a cuboctahedral arrangement. (d) Latent cuboctahedron (balls and sticks) in an ideal dodecahedron (sticks).

in **4**) but their centers retain the octahedral symmetry. These are precisely the edges that are shared between neighbouring icosahedra resulting in a perfect cubic packing (see Fig. S2, ESI‡) in spite of the symmetry loss of the Cs_{12} icosahedra.

3

4

Even in some cases in which an icosahedral cluster does not crystallize in a cubic space group, we see that the crystal structures are nearly cubic. For those systems we analyze the centroids of such clusters and calculate the shape measure of the polyhedron formed by the nearest neighbours (Table 3). We find them to have the practically perfect shapes expected for cubic crystal structures: a cuboctahedron for a face centered cubic (fcc) packing, a cube for a body centered (bcc) packing and an octahedron for a primitive cubic lattice. Three specific cases are worth a more detailed comment. One case is that of a Mo_{132} compound that showcases a beautiful nanodroplet formed by one hundred molecules of water organized in three nested icosahedral polyhedra.[48] While it does not crystallize in a cubic space group as does a related Mo_{132} complex shown in Table 2, but in the trigonal $R\bar{3}m$ group, the packing of the nanodroplets and the surrounding Mo_{132} units corresponds to a nearly perfect fcc structure, as indicated by a cuboctahedral shape measure of the twelve nearest neighbours of 0.001 (see Fig. S3, ESI‡). The second remarkable case corresponds to the complex structure composed by icosahedral clusters in the Ag_{188} compound reported by Fenske and co-workers,[49] which crystallizes in a space group with very low symmetry ($P\bar{1}$), but is still pretty close to an fcc structure, with S(cuboctahedron) = 0.10 for the twelve nearest neighbours. The third case is that of a $Fe_{30}Mo_{72}$ capsule built around a PMo_{12} Keggin unit.[50] In that compound, successive shells show tetrahedral (phosphate), octahedral (Mo_{12} cuboctahedron) and icosahedral (Fe_{30} icosidodecahedron, Mo_{12} icosahedron and Mo_{60} rhombicosidodecahedron) symmetries. Finally, even if the space group in which this compound crystallizes (*Cmca*) is not cubic, the icosahedral envelope gives a quite regular cubic fcc packing (cuboctahedral shape measure of 0.06 for the twelve nearest neighbors).

It is to be noted that in those structures with several concentric icosahedral clusters, such as $Li_{13}Cu_6Ga_{21}$ and the related $Na_{13}(Cd_{1-x}Tl_x)_{27}$, the outermost icosahedron loses a significant part of its fivefold symmetry, probably due to the onset of interactions with the surroundings of cubic symmetry, whereas the inner polyhedra are practically unaffected by the cubic packing and retain the full icosahedral symmetry. A

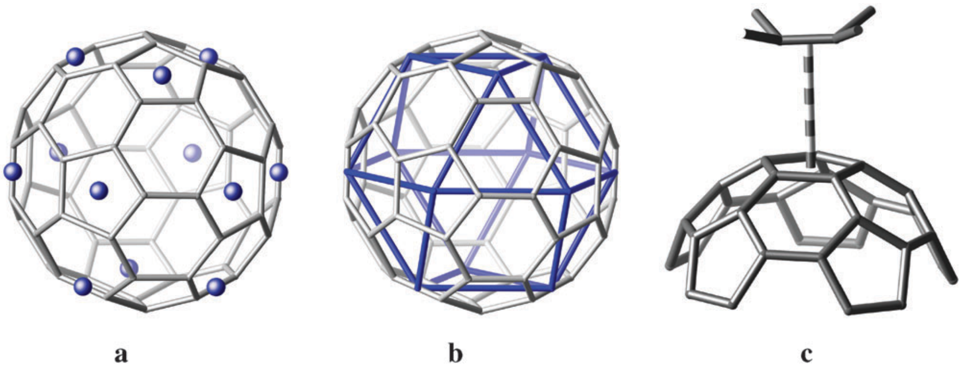

Fig. 8 Molecular structure of Buckminsterfullerene, C_{60} (a),[22,23] showing the centers of six pentagonal faces and of six edges that form a cuboctahedron (b). These are the points for the shortest intermolecular contacts with nearest neighbours (striped stick in (c) that account for a cubic crystal structure.

similar situation, but to a lesser degree, is found in dodecahedrane and in the caesium salt of the dodecaborane anion, in which the outer polyhedra of hydrogen atoms involved in intermolecular interactions are slightly distorted from the dodecahedron and the icosahedron, respectively, whereas the inner carbon or boron clusters form practically perfect icosahedral polyhedra. In the potassium salt of the same borane anion, though, the icosahedral symmetry of the hydrogen atoms seems to be not perturbed by intermolecular interactions, and probably a study of a larger number of examples would be needed before a clear statement can be made about the effect of cubic packing on concentric icosahedral polyhedra.

Conclusions

The discussion above clearly shows that there are some implicit relationships between the high symmetry point groups I_h and O_h that cannot be expressed through symmetry group–subgroup hierarchies. Those relationships are present in all the ideal Platonic and Archimedean polyhedra and a variety of chemical manifestations in nested polyhedral molecules or clusters of extended structures have been presented here. While the usual idea is that nested polyhedra must have the same symmetry, this situation occurs only when a full set of elements of a polyhedron (faces, edges or vertices) is augmented to form the next shell. In contrast, we have shown that polyhedra with cubic symmetry develop by partial augmentation of an inner shell of icosahedral symmetry and *vice versa*.

The relationship between octahedral and icosahedral polyhedra is extensively reflected in the cubic packing of a variety of icosahedral molecules or clusters in the solid state. The incompatibility between the icosahedral point group and crystallographic symmetry is nicely explained by O'Keefe and Hyde in the following terms:[35] "Strictly regular icosahedra are incompatible with crystallographic symmetry (which precludes the presence of 5-fold axes); but nature is very clever at designing periodic structures that feature *almost* regular icosahedra." The shape and symmetry analysis presented here suggests an alternative chemical view of this problem: *When molecules with icosahedral symmetry establish intermolecular interactions using their latent octahedral symmetry, they crystallize in a cubic or nearly cubic crystal system.*

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