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Keeping the Ball Rolling: Fullerene-like Molecular Clusters

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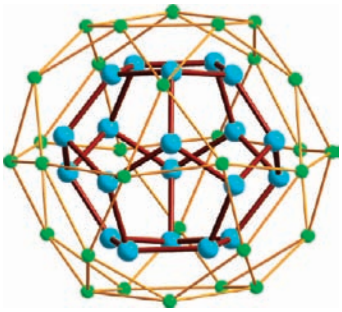

The discovery of fullerenes in 1985 opened a new chapter in the chemistry of highly symmetric molecules. Fullerene-like metal clusters, characterized by (multi)-shell-like structures, are one rapidly developing class of molecules that share this shape. In addition to creating aesthetically pleasing molecular structures, the ordered arrangement of metal atoms within such frameworks provides the opportunity to develop materials with properties not readily achieved in corresponding mononuclear or lower-nuclearity complexes.

In this Account, we survey the great variety of fullerene-like metal-containing clusters with an emphasis on their synthetic and structural chemistry, a first step in the discussion of this fascinating field of cluster chemistry. We group the compounds of interest into three categories based on the atomic composition of the cluster core: those with formal metal−metal bonding, those characterized by ligand participation, and those supported by polyoxometalate building blocks. The number of clusters in the first group, containing metal−metal bonds, is relatively small. However, because of the unique and complex bonding scenarios observed for some of these species, these metalloid clusters present a number of research questions with significant ramifications. Because these cores contain molecular clusters of precious metals at the nanoscale, they offer an opportunity to study chemical properties at size ranges from the molecular to nanoscale and to gain insights into the electronic structures and properties of nanomaterials of similar chemical compositions.

Clusters of the second type, whose core structures are facilitated by ligand participation, could aid in the development of functional materials. Of particular interest are the magnetic clusters containing both transition and lanthanide elements. A series of such heterometallic clusters that we prepared demonstrates diverse magnetic properties including antiferromagnetism, ferrimagnetism, and ferromagnetism. Considering the diversity of their composition, their distinct electronic structures, and the disparate coordination behaviors of the different metal elements, these materials suggest abundant opportunities for designing multifunctional materials with varied structures.

The third type of clusters that we discuss are based on polyoxometalates, in particular those containing pentagonal units. However, unlike in fullerene chemistry, which does not allow the use of discrete pentagonal building blocks, the metal oxide-based pentagonal units can be used as fundamental building blocks for constructing various Keplerate structures. These structures also have a variety of functions, including intriguing magnetic properties in some cases. Coupled with different linking groups, such pentagonal units can be used for the assembly of a large number of spherical molecules whose properties can be tuned and optimized.

Although this Account focuses on the topological aspects of fullerene-like metal clusters, we hope that this topical review will stimulate more efforts in the exploratory synthesis of new fullerene-like clusters. More importantly, we hope that further study of the bonding interactions and properties of these molecules will lead to the development of new functional materials.

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1. Introduction

A seminal discovery was made in 1985 when Curl, Krato, and Smalley reported C_{60},[1] an all-carbon molecule consisting of 12 pentagons and 20 hexagons arranged into a truncated icosahedron, the same configuration as seen on a soccer ball (Figure 1). It is also known as buckminsterfullerene, or just fullerene for short, due to its resemblance to the geodesic dome designed by visionary architect Buckminster Fuller.

Considered by chemists to be "the most beautiful molecule" because of its high symmetry, the molecular aesthetics of C_{60} has inspired and guided many innovative ideas in creating noncarbon molecules of comparable or even more complexity and in developing principles underlying their formation.[2−16] Such efforts have resulted in the production of a great variety of highly symmetric molecules, in particular cluster compounds of metal elements, many of which display novel bonding features and unusual properties[2−6,17] in addition to their structural beauty.[18]

In light of such recent exciting developments, an Account of these structurally unique and functionally stimulating species seems timely. Herein we survey the many molecular metal clusters that are characterized by a discrete, (multi)shell-like core structure, with or without ligand participation. Special attention will be paid to fullerene-like species, those possessing exactly 12 pentagonal rings in their core structure.

The clusters of our interest may be organized into three different groups according to the elemental makeup of their core. Clusters of the first type are characterized by a formal metal−metal-bonded fullerene-like core, while those in the second group possess nonmetal elements, either as an integral part of the fullerene-like core skeleton or as mediating ligands between the metal atoms that form the fullerene-like core. Clusters of the third type are constructed using polyoxometalate (POM) polyhedra. Herein, the salient structural features of these clusters will be discussed, and as appropriate, so will be the critical dependence of their identity on synthetic conditions. The current status of the research including the outstanding challenges will be elaborated toward the end, together with some personal perspectives for future development.

FIGURE 1. A perspective view of the soccer-ball-like structure of buckminsterfullerene C_{60} showing 12 pentagons and 20 hexagons of carbon atoms.

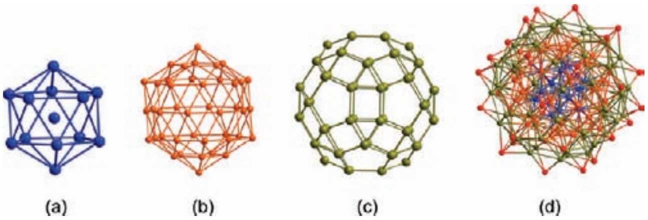

FIGURE 2. Anatomy of the multishell structure of $Pd_{145}(CO)_x(PEt_3)_{30}$ ($x \approx 60$): (a) shell 1, a 12-Pd icosahedron that encages a Pd atom; (b) shell 2, a 42-Pd ν_2 icosahedron; (c) shell 3, a 60-Pd rhombicosidodecahedron; (d) the structure of the multishell core shown with the square face-capping $Pd(PEt_3)$ ligands. The ethyl groups are removed for clarity.

2. Clusters Characterized by Fullerene-like Metal−Metal-Bonded Cores

The number of clusters characterized by fullerene-like, metal−metal-bonded cores is small. This may be due to the large number of highly reactive surface atoms present in such a core and the natural tendency for core growth, a process to lower the fraction of the surface metal atoms and eventually afford bulk metallic materials. If the growth is "arrested" with the use of suitable surface-passivating ligands, metal nanoparticles can be obtained. However, growth termination to achieve *nanoscopic yet molecular* clusters with well-defined structures and chemical compositions remains a grand challenge.

2.1. Fullerene-like Cluster Cores via Bonding Interactions between Transition Elements. The giant cluster $Pd_{145}(CO)_x(PEt_3)_{30}$ ($x \approx 60$) (**1**) is the first example of molecular cluster featuring a fullerene-like, metal−metal-bonded core.[19] Crystallographic analysis revealed a three-shell, 145-Pd core. The innermost shell (shell 1) is a Pd-encapsulating icosahedron of 12 Pd atoms. The polyhedral core, constructed from 20 equivalent triangular faces (Figure 2a), belongs to one of the five regular Platonic solids. The second shell (shell 2), encaging shell 1, contains 42 Pd atoms that are organized into a ν_2 icosahedron (where ν_2 denotes $2 + 1 = 3$ equally spaced atoms on each of the 30 edges) (Figure 2b). This shell is itself encapsulated by shell 3, the outermost shell of a 60-Pd rhombicosidodecahedron, one of the 13 Archimedean polyhedra (Figure 2c) and an isomer of the truncated icosahedron to which the C_{60} molecule belongs.[1,20] In addition to the char-

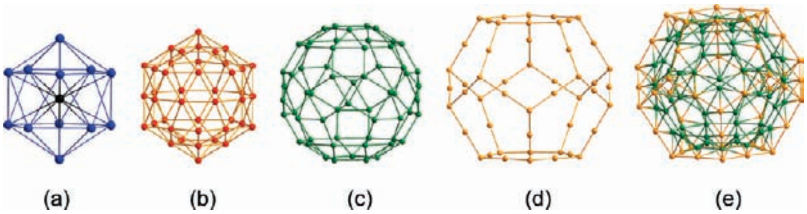

FIGURE 3. Anatomy of the multishell structure of (μ_{12}-Pt)$Pd_{164-x}Pt_x(CO)_{72}(PPh_3)_{20}$ ($x \approx 7$): (a) shell 1, a 12-atom Pt_xPd_{12-x} ($x \approx 1.2$) shell that encages a central μ_{12}-Pt atom; (b) shell 2, a 42-atom Pt_xPd_{42-x} ($x \approx 3.5$) ν_2 icosahedron; (c) shell 3, a 60-atom Pt_xPd_{60-x} ($x \approx 2.2$) rhombicosidodecahedron; (d) shell 4, a 50-Pd ν_2 pentagonal dodecahedron; (e) the structure of the multishell core.

acteristic 12 pentagonal faces, there are 20 triangular and 30 square faces in a rhombicosidodecahedron. The term "Keplerate" was used first by Müller et al. to describe this particular type of structure that contains both Platonic and Archimedean solids, one inside another.[2,3]

Each of the 30 squares is capped by a PEt_3-ligated Pd atom. It is presumed that one-half of the square basal Pd atoms are edge-bridged by CO molecules, but these small ligands cannot be positioned accurately due to crystallographic disorder (Figure 2d).

A 165-metal heterometallic cluster (μ_{12}-Pt)$Pd_{164-x}Pt_x(CO)_{72}(PPh_3)_{20}$ ($x \approx 7$) (**2**) has recently been reported.[6] The cluster core consists of a kernel Pt atom encapsulated by four concentric shells. Moving from the innermost to the outermost one, shells 1−4 contain 12, 42, 60, and 50 metal atoms, respectively. The atomic arrangements in shells 1−3 are identical to those of **1** (Figure 3a−c). Shell 4 is a ν_2 pentagonal dodecahedron, a regular Platonic solid containing 20 vertices with the midpoint of each of its 30 edges occupied by an additional Pd atom (Figure 3d). Each of the vertex Pd atoms caps a triangular face of shell 3, while each of the edge-middle-occupying Pd atoms is situated above the square faces of shell 3. Interestingly, this Pd_{50} architecture is the sole ν_2 pentagonal dodecahedron hitherto known. Its 20 vertices are coordinated by PPh_3 ligands that provide steric shielding for the multishell core. Cluster stabilization is also provided by 72 bridging CO ligands between shells 2 and 3 and between shells 3 and 4.

2.2. Fullerene-like Cluster Cores Formed by Bonded Main-Group Metals. Since the report of $[Al_2\{CH(SiMe_3)_2\}_4]$, the first molecular complex characterized with a two-electron−two-center Al−Al bond,[21] a number of clusters featuring similar metal−metal bonding interactions have appeared in the literature.[22−27] These include the anionic clusters of $[Al_{69}R_{18}]$,[25] $[Al_{77}R_{20}]$,[26] and $[Ga_{84}R_{20}]$[27] [$R = N(SiMe_3)_2$], and neutral species such as $Si@Al_{56}[N(2,6\text{-}iPr_2C_6H_3)SiMe_3]_{12}$[28] and $Al_{50}(Cp^*)_{12}$ (**3**, $Cp^* = C_5Me_5$).[29] Although each of these clusters possesses a spherical multishell core, only that of $Al_{50}(Cp^*)_{12}$ displays a fullerene-like structure (Figure 4a).

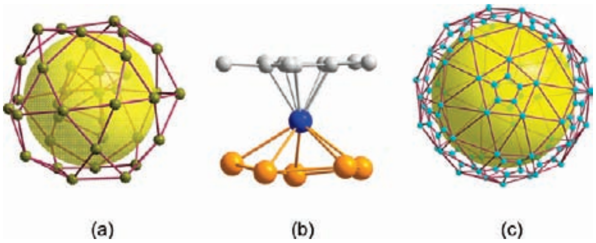

FIGURE 4. (a) Ball and stick model of the Al_8 core and the surrounding icosidodecahedral Al_{30} shell, (b) the "mixed sandwich" coordination of each of the outer 12 Al atoms through η^5-$C_5(CH_3)_5$ and η^5-Al_5, and (c) polyhedral representation of the carbon shell of $Al_{50}Cp^*_{12}$.

The double-shell core can be viewed as a distorted square antiprism of 8 Al atoms encapsulated by an outer 30-Al icosidodecahedron whose 12 pentagonal faces are each capped by an AlCp* moiety. As such, each of these latter Al atoms, sandwiched between a Cp* ring and an Al-based pentagon, is decacoordinate (Figure 4b). This arrangement results in the 12 Al atoms in the AlCp* units forming a regular icosahedron, while the 60 CH_3 substituents of the Cp* ligands form a surface topology reminiscent of a "distorted fullerene". Different from the Archimedean polyhedron of fullerene characterized by 12 pentagonal and 20 hexagonal faces with 60 vertices and 90 edges, the 20 hexagonal faces in $Al_{50}(Cp^*)_{12}$ are divided into 80 trigonal faces, which, together with the 12 pentagonal faces, form a snub dodecahedron with 60 vertices and 150 edges. The 60 carbon atoms of the C_5 units are located within each of the 12 pentagonal faces (Figure 4c). The above structural description also fits the definition of a "Keplerate".

It has become clear from the structural elucidation of clusters **1**−**3**, detailed in the preceding, that a fullerene-like shell encapsulating an icosahedron is a common phenomenon. Similar observations are also made in $Al_{12}[AlBr_2(THF)]_{10} \cdot 2THF$ (**4**)[30] and $[Ga_{24}Br_{18}Se_2] \cdot 12THF$ (**5**).[31] For **4**, except for the two *trans*-disposed and THF-coordinated Al vertices, each of the remaining 10 Al atoms is bonded to one $[AlBr_2(THF)]$ unit (Figure 5a). The 20 bromine atoms are so positioned that each is situated above a triangular face of the icosahedron. A distorted pentagonal dodecahedron of bromine atoms thus

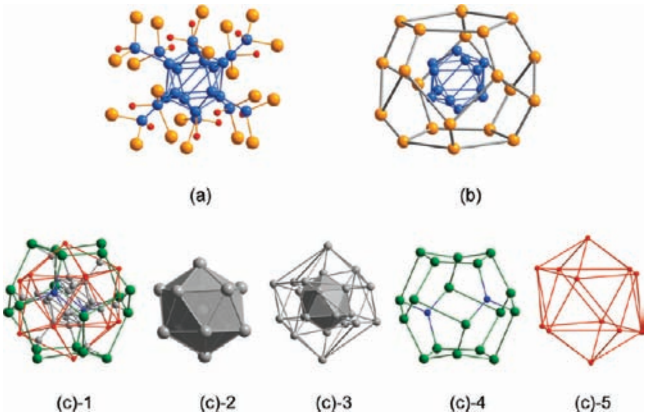

FIGURE 5. The structure of $Al_{12}[AlBr_2(THF)]_{10} \cdot 2THF$ (a); only the O atoms of THF molecules are shown for clarity. A distorted pentagonal dodecahedron of bromine atoms encapsulating a regular icosahedron of Al atoms (b) is shown. The crystal structure of $[Ga_{24}Br_{18}Se_2] \cdot 12THF$ (Ga gray, Br green, Se red, O yellow) is represented as follows: (c-1) the overall structure of $Ga_{24}Br_{18}Se_2O_{12}$ moiety; (c-2) the inner Ga_{12} icosahedron; (c-3) the outer Ga_{12} icosahedron; (c-4) the pentagonal dodecahedron of $Br_{18}Se_2$; (c-5) the icosahedron formed by 12 THF O atoms.

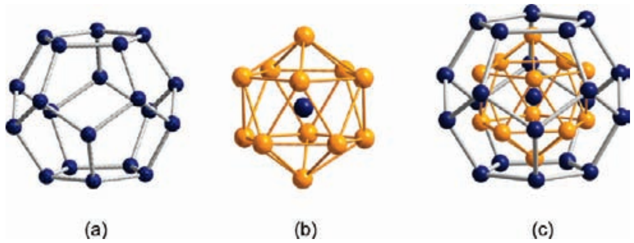

FIGURE 6. Ball-and-stick drawings of (a) the As_{20} subunit, (b) the $[Ni_{12}(\mu_{12}\text{-}As)]^{3-}$ subunit, and (c) the $[As@Ni_{12}@As_{20}]^{3-}$ ion.

results (Figure 5b). For **5**, there is an icosahedral core of Ga_{12} encaged by an outer distorted 12-Ga icosahedron and a dodecahedron formed by 18 Br and 2 Se atoms (Figure 5c).

Although there is nothing in common with the Al clusters discussed above, the onion-like $[As@Ni_{12}As_{20}]^{3-}$ cluster ion (**6**)[4] is included here to further illustrate the prevalence of the fullerene-like double-shell structure, which is characterized by a pentagonal dodecahedron (As_{20}, Figure 6a) encapsulating an icosahedron (Ni_{12}, Figure 6b). Interestingly, like C_{60}, the HOMO and LUMO of $[As@Ni_{12}As_{20}]^{3-}$ are 5-fold-degenerate with h_u and h_g symmetries, and its lowest singlet excitation is optically forbidden.[32]

3. Clusters Possessing Fullerene-like Cores Involving Nonmetal Elements

Numerous polynuclear metal complexes have been reported, many of which possess well-defined polyhedral core structures with the involvement of ligand atoms. The meaning of "ligand involvement" is 2-fold: in one the ligand, as a whole or in part, is an integral part of the polyhedral core, whereas in the other, the polyhedral cores are composed of only metal atoms, nonetheless mediated by the ligands. Notable examples include cluster complexes of Ag,[33,34] Fe,[35] Mn,[36−38] Cu,[39−41] and lanthanide elements.[42] Significant progress notwithstanding, complexes displaying fullerene-like core structures remain scarce.

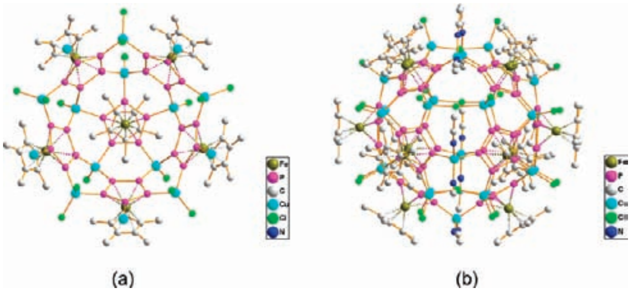

FIGURE 7. (a) The structure of the half-shell component of **7** featuring one central and five peripheral $[Cp^*Fe(\eta^5\text{-}P_5)]$ units arranged into a bowl-shaped structure via $(CuCl){-}P_3$ coordination and (b) the spherical structure of **7** composed of two half shells joined together by five $[Cu_2Cl_3]^-$ and five $[Cu(CH_3CN)_2]^+$ units.

3.1. Clusters with Fullerene-like Cores Containing Both Metal and Nonmetal Elements. Scheer and co-workers reported a C_{60}-like cluster complex $[\{Cp^*Fe(\eta^5{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}P_5)\}_{12}\{CuCl\}_{10}\{Cu_2Cl_3\}_5\{Cu(CH_3CN)_2\}_5]$ (**7**)[10] obtained by reacting pentaphosphaferrocene $Cp^*Fe(\eta^5\text{-}P_5)$ with CuCl.

The crystal structure of **7** is depicted in Figure 7. It can be viewed as two bowl-shaped half-shells of $[\{Cp^*Fe(\eta^5{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}P_5)\}_6\{CuCl\}_5]$ stitched together by five $[Cu_2Cl_3]^-$ and five $[Cu(CH_3CN)_2]^+$ units. The construction of the half-shell can be achieved formally by organizing five identical $[Cp^*Fe(\eta^5\text{-}P_5)]$ units around a central unit of the same kind via five sets of $(CuCl){-}P_3$ coordination, with the central and two peripheral $[Cp^*Fe(\eta^5\text{-}P_5)]$ units each contributing one P atom. The framework features five- (P_5) and six-membered rings (Cu_2P_4) alternating in a fashion (Figure 7b) analogous to the celebrated C_{60} molecule. The isostructural bromo analogue of **7**, $[\{Cp^*Fe(\eta^5{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}P_5)\}_{12}\{CuBr\}_{10}\{Cu_2Br_3\}_5\{Cu(CH_3CN)_2\}_5]$ (**8**), was also obtained.[43]

3.2. Clusters with Fullerene-like Cores Composed of Ligand-Bridged Metal Atoms. Much different from **7** and **8** whose fullerene-like cores are constructed using both the metal and ligand atoms, polynuclear heterometallic complexes characterized by the existence of metal-only fullerene-like core structures have been reported recently. One such species, synthesized under hydrothermal conditions using an aqueous mixture of $Ni(NO_3)_2$, $La(NO_3)_3$, and iminodiacetic acid (H_2IDA),[5] is structurally shown in Figure 8a.

The cluster core of compound **9**, $[La_{20}Ni_{30}(IDA)_{30}(CO_3)_6(NO_3)_6(OH)_{30}(H_2O)_{12}] \cdot (CO_3)_6 \cdot 72H_2O$, features a fascinating

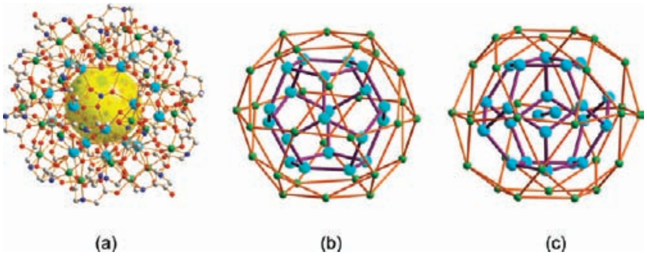

FIGURE 8. (a) Crystal structure of **9** with H atoms and the counterion CO_3^{2-} removed for clarity, (b) core structure of **9** showing an outer Ni_{30} icosidodecahedron encaging an inner La_{20} dodecahedron, and (c) cluster core structure of $La@La_{20}@Ni_{30}$ showing a hydrated La(III) ion internalized in the decanuclear cage. Color legends: Ni, green; La, cyan; C, gray; N, blue; O, red.

double-sphere structure of the Keplerate type (Figure 8b). The 30 outer-sphere Ni atoms span an icosidodecahedron, while the 20 inner-sphere La atoms occupy the vertices of a perfect dodecahedron. The cage-like arrangement of the two distinct sets of metal ions manifests the beauty of symmetry as both ideally possess icosahedral symmetry, the highest possible symmetry for molecules.[44]

The cluster identity is dependent on the starting Ln/Ni/IDA ratio as well as the lanthanide ion. Increasing the amount of $La(NO_3)_3$ leads to a 3D assembly of cluster building blocks connected by units of $Na(NO_3)/La(NO_3)_3$; the building block resembles closely the core of **9**, with a hydrated La(III) ion internalized in the decanuclear cage being an extra feature (Figure 8c). This unique La atom is connected to the La atoms within the dodecahedron via three bridging carbonato ligands.[18]

The use of different lanthanide starting materials caused profound changes to the identity of cluster products. With the use of $(Pr/Nd)(NO_3)_3$, isostructural complexes $[Ln_{20}Ni_{21}(IDA)_{21}(OH)_{24}(C_2H_2O_3)_6(C_2O_4)_3(NO_3)_9(H_2O)_{12}](NO_3)_9$ (**10**, Ln = Pr; **11**, Ln = Nd; $C_2H_2O_3$ is the alkoxide form of glycolate) possessing a core of an outer shell of 21 Ni atoms encapsulating an inner shell of 20 Ln atoms were obtained.[18] The dual-shell core of $Ln_{20}@Ni_{21}$ (Ln = Pr, Nd) can be formally transformed from that of **9** (Figure 9). By removal of nine uniquely positioned Ni atoms from the outer Ni shell of **9**, followed by a rotation of 60° of the red-colored set of Ni atoms with respect to the green-colored set, the Ni_{21} framework of $Ln_{20}@Ni_{21}$ is generated (top pathway, Figure 9). To obtain the inner Ln_{20} core from the dodecahedron of La of **9**, a proper C_6 rotation of the red-colored fragment with respect to the light-blue set is adequate (bottom pathway, Figure 9).

Synthesis using $Gd(NO_3)_3$ under otherwise identical conditions afforded the highly sophisticated 108-metal complex $[Gd_{54}Ni_{54}(IDA)_{48}(OH)_{144}(CO_3)_6(H_2O)_{25}](NO_3)_{18}\cdot(H_2O)_{140}$ (**12**, Figure 10a) whose core,[45] abbreviated as $Gd_2Ni_6@Gd_{20}@Gd_{32}@Ni_{48}$, can be described as a nesting-doll-like multishell (Figure 10b).

The latest development is the production, under ambient pressure, of a four-shell 136-metal cluster complex $[La_{60}Ni_{76}(IDA)_{68}(OH)_{158}(NO_3)_4(H_2O)_{44}](NO_3)_{34}\cdot(H_2O)_{42}$ (**13**, Figure 10c) with a core of $Ni_8@La_{20}Ni_4@La_{40}@Ni_{64}$ that approximates a rectangular parallelepiped (Figure 10d).[46]

These latter multishell clusters do not belong to the fullerene-type clusters according to our definition above. However, together with those that are, they not only illustrate the sensitive dependence of the cluster identity on reaction conditions but also provide guidelines for identifying suitable synthetic conditions in order to realize clusters of a certain type, including those that are fullerene-like.

In this context, the lanthanide cluster complex $[Er_{60}(\text{threonine})_{34}(\mu_6\text{-}CO_3)_8(\mu_3\text{-}OH)_{96}(\mu_2\text{-}O)_2(H_2O)_{18}]Br_{12}(ClO_4)_{18}(H_2O)_{40}$ (**14**)[47] is also of note (Figure 11a). The 60 Er atoms are organized into 24 $Er_4(\mu_3\text{-}OH)_4$ units, each represented as a tetrahedron or a sphere in Figure 11b. These cubane units are joined together by sharing corners with three identical neighbors, forming a discrete sodalite cage composed of six squares and eight hexagons of the cubane units.

Alternatively, the cluster core may be viewed as double shell with its outer shell of 24 metal atoms encasing an inner shell of 36 metal atoms (Figure 11c). The outer sphere is a truncated octahedron, while the inner shell is a nonstandard convex polyhedron composed of 24 triangles, 6 squares, and 8 hexagons; it can be achieved by truncating a truncated octahedron (doubly truncated octahedron). Interestingly, this polyhedron is not one of the Platonic, Archimedean, or Johnson solids.

4. Fullerene-like Clusters Formed by POM Polyhedra

POM-based fullerene-like clusters significantly outnumber the aforementioned non-POM types of clusters. Similar to metal complex-based clusters, that is, the second type of cluster species described above, various POM-supported fullerene-like clusters may also be discussed according to whether the fullerene-like core involves ligand participation in addition to the basic POM units.

4.1. Fullerene-like Clusters Constructed by Both POM and Ligand Polyhedra. Only one example of fullerene-like cluster complex formed through both POM and ligand polyhedra exists in the literature.[48] The anionic cluster $[(VO)_{12}(\mu_2\text{-}OH)_{12}(\mu_3\text{-}PhPO_3)_8]^{4-}$ (**15**) has a dodecahedral core composed of pentagonal $(VO)_3(PPh)_2$ units (Figure 12). The two P atoms

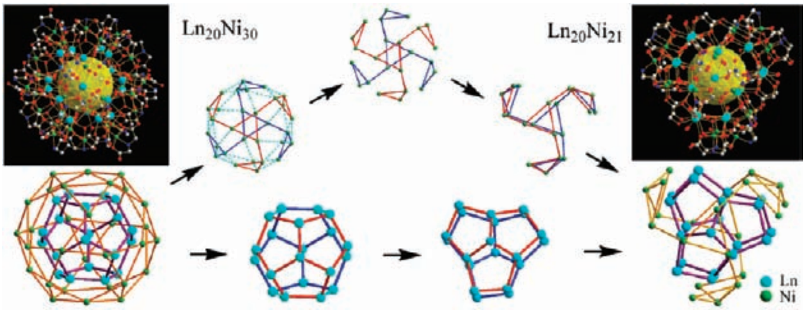

FIGURE 9. Depiction of the formal transformations toward the making of the inner and outer frameworks of $Ln_{20}@Ni_{21}$ from respective polyhedra of **9**.

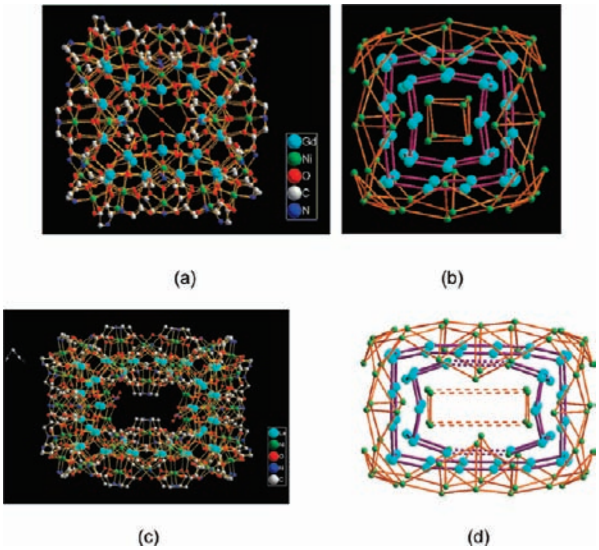

FIGURE 10. Ball-and-stick views of the cluster cores (a) $Gd_2Ni_6@Gd_{20}@Gd_{32}@Ni_{48}$ and (c) $Ni_8@La_{20}Ni_4@La_{40}@Ni_{64}$ and their respectively metal-only framework structures [b and d].

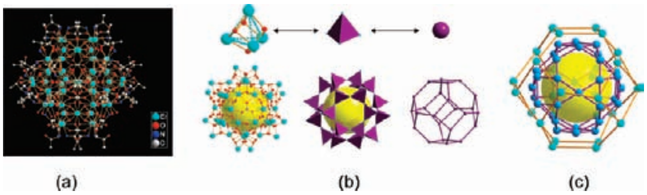

FIGURE 11. (a) Crystal structure of the cationic cluster of $[Er_{60}(\text{threonine})_{34}(CO_3)_8(\mu_3\text{-}OH)_{96}(\mu_2\text{-}O)_2(H_2O)_{18}]^{30+}$, (b) the 60 Er atoms organized into 24 $Er_4(\mu_3\text{-}OH)_4$ units (represented as a tetrahedron or a sphere) joined together by sharing corners with three identical neighbors to form a sodalite cage, and (c) an alternative view of Er_{60} core with an outer shell of 24 Er atoms (cyan) encapsulating an inner shell of 36 Er atoms (blue).

are nonadjacent, and in the middle of each P−V edge sits a bridging O atom. The two adjacent V atoms within a particular pentagon are doubly bridged by hydroxo ligands, and each V atom is terminally coordinated by an oxo group.

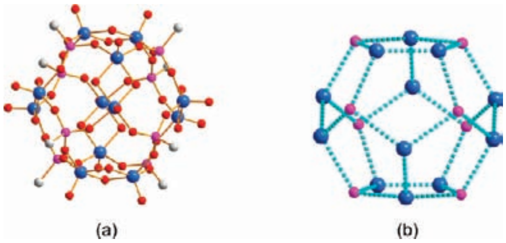

FIGURE 12. (a) Perspective plot of $[(VO)_{12}(\mu_2\text{-}OH)_{12}(\mu_3\text{-}PhPO_3)_8]^{4-}$ anion with the phenyl groups omitted for clarity and (b) a drawing of the dodecahedral arrangement of the 12 V atoms and 8 P atoms. Color legends: P, purple; V, blue; O, red; C, gray.

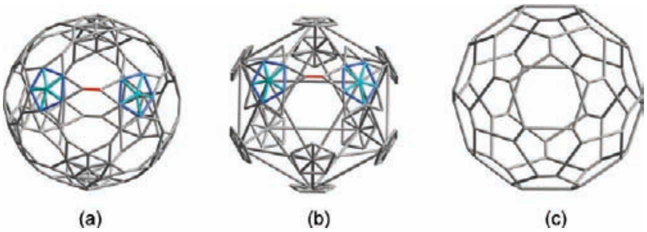

FIGURE 13. Depiction of the 132-Mo fragment of **16** with its spherical architecture highlighted (a). Two $[(Mo)Mo_5](Mo^V)_5$ units (blue and cyan) linked by a $Mo^V{-}O{-}Mo^V$ bridge (red) are highlighted (b). The outer corners of a $[(Mo)Mo_5](Mo^V)_5$ unit are linked to the Mo centers of the $Mo^V{-}O{-}Mo^V$ bridges. Shown in panel c is the structure of the truncated icosahedron of the 60 Mo linker atoms with 12 regular pentagons and 20 trigonal hexagons showing its coherence to the C_{60} fullerene.

4.2. Fullerene-like Clusters Composed of Metal-Oxide Polyhedra only. Different from **15** whose fullerene-like cluster core consists of both VO and PO polyhedra, the core of $[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(MeCO_2)_{30}(H_2O)_{72}]^{42-}$ (**16**) is constructed exclusively from MoO-type polyhedra (Figure 13).[49] Alternatively, **16** can be formulated as $\{[Mo_2{}^VO_4(CH_3CO_2)]\}_{30}\{(Mo)Mo_5O_{21}(H_2O)_6\}_{12}]^{42-}$ to highlight its modular structure and the corresponding building blocks, 12 $\{(Mo^{VI})(Mo^{VI})_5\}$ pentagons and 30 $\{Mo_2{}^V\}$ dumbbells. The pentagonal $\{(Mo^{VI})(Mo^{VI})_5\}$ unit is constructed by linking five $\{MoO_6\}$ octahedra to a central pentagonal bipyramidal $\{MoO_7\}$ unit via bridging O atoms. Each $\{Mo_2{}^V\}$ dumbbell unit links two $\{MoO_6\}$ octahedra from different $\{(Mo^{VI})(Mo^{VI})_5\}$ units, generating a spherical structure (Figure 13a) wherein the 12 Mo_6O_{21} pentagons occupy the vertices of an icosahedron (Figure 13b), while the 30 $\{Mo_2{}^V\}$ dumbbells span a truncated icosahedron with 12 regular pentagons and 20 hexagons of trigonal symmetry (Figure 13c).

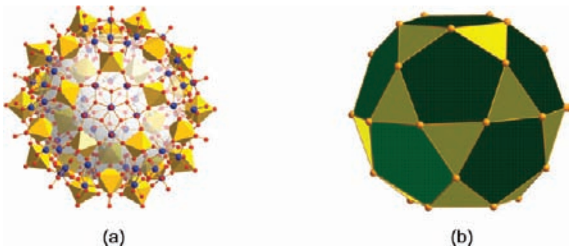

FIGURE 14. (a) Structure of **17** emphasizing the octahedral FeO_6 linkers (yellow) within the metal-oxide skeleton (Mo, blue; O red spheres) and (b) the Fe atoms (small colored spheres) of the $\{(Mo^{VI})Mo_5{}^{VI}\}_{12}\{Fe^{III}\}_{30}$ cluster spanning an icosidodecahedron.

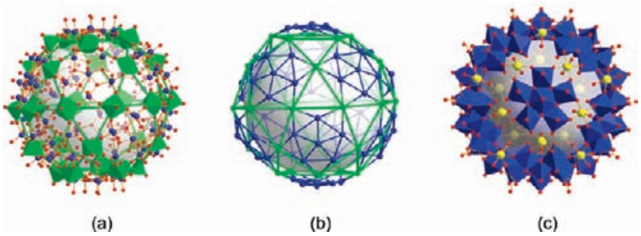

FIGURE 15. (a) Structure of $[(Mo^{VI})Mo_5{}^{VI}]_{12}(OV^{IV})_{30}$ (**19**) with the OV^{IV} units within the metal-oxide skeleton (Mo, blue; O, red spheres) highlighted in green, (b) the $(OV^{IV})_{30}$ (green) in **19** spanning an icosidodecahedron, and (c) the structure of $\{(Mo)Mo_5\}_{12}\{Cr^{III}\}_{30}$ (**20**), with the basic pentagonal units highlighted as blue polyhedra; the 30 Cr^{III} linker centers (Cr yellow, O red) are each in an octahedral environment.

Significantly, when **16** was reacted with $FeCl_3$, the 30 $Mo_2{}^V$ dumbbell units were fully replaced by $Fe^{III}(H_2O)$ polyhedra, affording a Keplerate-type molecular cluster **17** whose 30 Fe^{III} centers span an icosidodecahedron (Figure 14);[50] each $Fe^{III}(H_2O)$ polyhedron bridges two MoO_6 octahedra from two pentagons of the Mo_6O_{21} unit.

A series of Keplerates of general formula $[(Mo)Mo_5]_{12}$-(linker)$_{30}$ [linker = Fe^{III} (**18**),[51] OV^{IV} (**19**) (Figure 15a,b),[52,53] and Cr^{III} (**20**) (Figure 15c)[54]] were obtained based on the deliberate generation of the pentagonal units. The mentioned fullerene-like clusters, possessing varying cavity size, share the common building block $[(Mo)Mo_5]$. Very recently, unprecedented and differently applicable pentagonal units of the type $[(W)W_5]$ were successfully applied to the building of a Keplerate structure of $[(W)W_5]_{12}\{Mo_2\}_{30}$ (**21**).[55,56] Although these pentagonal units are not stable in solution, they can be viewed as *transferable* building blocks for the construction of clusters with even a higher degree of structural sophistication. Apparently inspired is the recent report of applying planar five-connected nodal ligands in the construction of cage molecules that are topologically identical to the C_{60} fullerene structure.[57]

5. Summary and Outlook

As human beings, we are susceptible to beauty, and as chemists, we enjoy the luxury of coming across a large number of molecules and being able to recognize and appreciate their molecular aesthetics. Even better, we are inspired to develop molecular beauties of our own. The seminal discovery of fullerenes has certainly opened a new game in the search for highly symmetric molecules, not for the pursuit of mere aesthetics but more importantly for creating materials with unique properties and useful applications.

Years of unabated enthusiasm and efforts of synthetic and computational chemists have yielded a large number of metal cluster complexes characterized by shell-like structures, of which the unique subgroup featuring fullerene-like core structures is elaborated in this Account. Though frequently the outcome of serendipitous discoveries, studies of such clusters have provided much needed insights into the possible mechanism(s) responsible for their assembly and new systems for the study of novel physical and chemical properties.

Surveyed herein are three distinct families of clusters, grouped according to their core make-ups, one with metal–metal bonding, the second involving ligand participation, and the third based on polyoxometalates. Their syntheses are rather sensitive to reaction conditions so that changing the conditions may lead to clusters of different nuclearity and altered structures. The richness of this synthetic and structural chemistry is manifested by the polyoxometalate family, for which thousands of different compounds have been obtained, and most of them can be easily prepared.[58,59] This is especially valid for spherical systems with the high formation tendency where a facile synthesis is known.[60] In the course of these endeavors, a number of well-defined cluster motifs have been identified, and their uses as building blocks for the construction of other types of clusters may be envisioned. While it is fair to predict that research activities in this particular direction of cluster chemistry will continue to grow with high possibility of discovering many interesting species, we note that the synthetic and structural chemistry can only be the very first step toward this fascinating and important field of cluster chemistry. Indeed, the discussion presented herein is entirely restricted to the topological aspects of the cluster species, in particular to that of the cluster core structure. It should be noted that the bonding interactions in the various clusters are vastly diverse and complex as suggested, for example, by the highly mixed-valent bonding situations observed for the Al and Ga clusters.[22−27] The studies of the unique and complex bonding interactions and potentially useful properties of these clusters, though challenging, should constitute a significant part of the future efforts in addition to further exploratory cluster synthesis. By this topical Account, we wish to share our excitement about these fascinating cluster species and offer our own small push to help move forward this beautiful chemistry.

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FOOTNOTES

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