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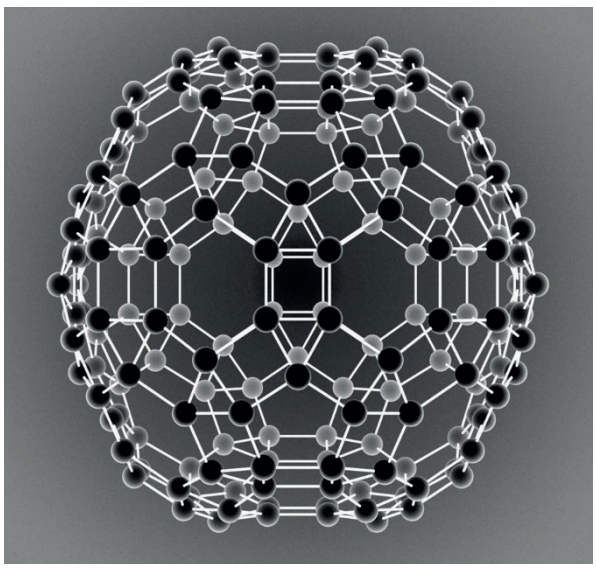
POLYNUCLEAR COMPLEXES

Buckyball's silver cousin

> We never expected to make a structure like {Ag_{180}}

Buckminsterfullerene occupies a special place in our chemical conscience. An archetypal icosahedral molecule, its 60 carbon atoms form a surface mosaic of 20 hexagons and 12 pentagons — the geometry we recognize as a football. The aesthetics of molecular polyhedra motivated Di Sun, Stan Schein and their colleagues to prepare almost 100 Ag clusters over the years, all the while hoping for one of exceptional geometry. The team noted that polygons — 3-, 4-, 5- and 6-gons in particular — routinely formed the faces of the clusters. "These observations reminded us of Platonic and Archimedean solids, which contain similar polygonal faces composing their surfaces," says Sun. "We believed that special polyhedra might be synthesized from these polygon units." Now, writing in *Proceedings of the National Academy of Sciences of the USA*, the team describes a {Ag_{180}} icosahedral cage with striking geometrical resemblance to the buckyball. A solvothermal reaction of $[Ag(^{i}PrS)]_n$ and $Ag(MeSO_3)$ in MeOH yielded crystals of the thiolate-capped Ag(I) complex salt $[Ag_{180}(^{i}PrS)_{90}(MeSO_3)_{44}](MeSO_3)_{46}\cdot 34MeOH$. Sun admits that the high symmetry of the cage took the team by surprise: "We never expected to make a structure like {Ag_{180}}."



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The choice of Ag(I) for the vertices is crucial to realizing the {Ag_{180}} cage, the diameter of the metal skeleton alone being 2.5 nm. In general, these $4d^{10}$ ions are not fussy, such that they can each assume a coordination number from 2 to 8 and give rise to a variety of structural motifs further enriched by the possibility of argentophilic interactions. Therefore, while Ag(I) centres can easily exist in the geometries necessary for the polyhedron, a more discerning ion such as Pd(II) — whose $4d^8$ electronic configuration overwhelmingly favours square planar coordination — can only form polyhedra when combined with bent ligands.

A pattern began to emerge when the Ag–Ag distances in the polyhedron were compared. Of the 360 Ag–Ag edges, 180 are between 3.00 and 3.14 Å in length, a range in which strong argentophilic interactions are possible. The remaining 180 Ag–Ag contacts are longer and much weaker. The strong interactions serve to stabilize {Ag_3} units — termed 'trigons' — such that they become the stable building block of the polyhedron. Indeed, the {Ag_{180}} structure can be viewed as 60 {Ag_3} trigons linked by weak argentophilic connections. Mass spectrometric analysis also underscored the importance of trigons, with the detection of ions assigned to $\{Ag_3\}_{60}$ species accompanied by a series of oligomers of the form $\{Ag_3\}_n$ (n = 1–10, excluding 3 and 9). The motifs observed by the team led them to propose a growth mechanism based on the sequential assembly of $\{Ag_3\}_n$ species, in which the {Ag_{180}} cage is built up from {Ag_3} trigons to $\{Ag_3\}_5$ pentatrigons to $\{Ag_3\}_{10}$ decatrigons. Finally, six decatrigons assemble into the {Ag_{180}} cage. Supporting the role of the decatrigon was the detection of $\{Ag_3\}_{10}$ ions by mass spectrometry upon dissolution of {Ag_{180}}.

The {Ag_{180}} cage appears complicated in that its surface is a tessellation of 60 trigons, 90 tetragons, 12 pentagons and 20 hexagons. But the cage is best thought of as $\{Ag_3\}_{60}$, and if we picture each trigon as a C atom, we would arrive at the familiar icosahedral structure of C_{60}, the buckyball. Using trigon chemistry to build highly symmetric Ag(I) cages likely does not end here. {Ag_{540}} and {Ag_{720}} cages are next on the agenda because, "both have icosahedral symmetry and follow the 'rules' that we came to appreciate from {Ag_{180}}", Schein explains. The diverse family of fullerene structures may inspire the synthesis of even more elaborate Ag cages, designed by simply replacing C atoms by {Ag_3} trigons.

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