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Carbon-Free Fullerenes: Condensed and Stuffed Anionic Examples in Indium Systems

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Condensed, well-ordered analogs of the fullerenes occur in the hexagonal phases $Na_{96}In_{97}Z_2$ (Z = nickel, palladium, or platinum). Large cages of In_{74} (D_{3h}) and M_{60} (= $In_{48}Na_{12}$, D_{3d}) share pentagonal faces to generate a double–hexagonal close-packed analog of NiAs. All these polyhedra are centered by partially disordered $In_{10}Z$ clusters within deltahedra of sodium atoms that cap all inner faces of the cages, namely, $Z@In_{10}@Na_{39}@In_{74}$ and $Z@In_{10}@Na_{32}@Na_{12}In_{48}$ "onions." The highest filled bands in these compounds apparently involve localized electron pairs on surface features on In_{74} -based layers. Structural and electronic relations between diamond and NaIn (stuffed diamond structure) parallel those between certain fullerenes and $Na_{96}In_{97}Z_2$ and, presumably, other valence-driven intermetallic phases.

The fullerenes C_{60} , C_{70} , and their derivatives that are generating so much interest and so many novel results (1, 2) naturally raise the question of whether similar "naked" cage species might be synthesized for other main-group elements. The strong π bonds formed by C must be a major factor in the kinetic stabilities of the fullerenes. whereas the possibility of heavier element analogs may be limited by the ease with which they rearrange to other more stable structures. Analogous ions naturally have different decomposition reactions (3). Important examples are the original Zintl phases NaTl, NaIn, and Li(Al,Ga,In) where the presumed anionic group-13 elements form a diamond lattice that is stuffed with the cations (4, 5). Recent studies indicate that Zintl's very simple isoelectronic analogy seems to have merit (6).

We report a remarkable alternative in In chemistry, fulleride-like species such as In_{74} that share pentagonal faces to form layers and are also stuffed with both centered $In_{10}Ni^{10-}$ -like clusters and Na deltahedra that screen the

would be described as Ni@In₁₀@Na₃₉@In₇₄ in the nomenclature of Smalley and co-workers (1, 7). Size proportions appear to be particularly important because substitution of either K or Ga for Na or In affords nothing comparable. Two series have been discovered: hexagonal $Na_{96}In_{97}Z_2$ (1) and orthorhombic $Na_{172}In_{197}Z_2$ (2), where Z may be Ni, Pd, or Pt (8). Members of both groups afford wellrefined, single-crystal x-ray definition of nearly all aspects of the structures to reveal In₇₀, In_{74} , and In_{78} fullerene-like cages as well as distinct $M_{60} = In_{48}Na_{12}$ polyhedra. These are in notable contrast to the rotationally disordered fullerene and fulleride solids for which characterization has relied heavily on nuclear magnetic resonance. The structure of 1 with Ni and Pd will be reported here (9, 10) together with a few relevant aspects of 2 containing Ni. The latter will be described elsewhere because of its 141 independent atoms and structural complexity (11).

clusters from the In cages. One principal array

The novel phases $Na_{96}In_{97}Z_2$ exhibit several features of note. The In_{74} cages of D_{3h} ($\delta m2$) symmetry (Fig. 1) have In– In distances of 2.92 to 3.05 Å, typical for delocalized bonding in smaller clusters In_n, where n = 11, 12, or 16 (12–17). The

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deployment of these and other unusual features in the cell is generalized in Fig. 2. All three-bonded In atoms gain at least one additional In neighbor, presumably to compensate for the absence of the good π bonding. Of the 12 pentagonal faces customary in fullerenes, the six in In₇₄ about the horizontal mirror plane (In2, 4, 7, 7, 4; Fig. 1) are shared with like cages to generate close-packed layers. Five such pentagons are shaded in Fig. 2. Each polyhedron has a diameter of 16.0 Å (the a axis) about the waist and 15.5 Å along the c axis versus ~ 7.1 Å for C₆₀. Space is filled with three additional features: (i) small surface units of In that augment bonding of atoms in In74 where intercage In-In interactions are not possible; (ii) specifically ordered and roughly spherical shells of endo- and exohedral Na on all cages; and (iii) seemingly identical cluster anions $In_{\sim 10}Z$ within both In_{74} (A) and in an interlayer region defined by M_{60} = In48Na12 (B) (see below). Inappropriate spatial and symmetry constraints provided by the (nonbonded) Na₃₉ and Na₃₂ polyhedra, which line the respective polyhedra, appear to preclude well-ordered In₁₀ units about the central Z. All other atoms in both the Ni and Pd compounds refined well.

Each of these three features will be described separately. First, additional intercage bonds form between like In5 and In6 atoms that adjoin the shared pentagons (Fig. 1), In5 in triangles between three In₇₄ and, at higher latitude, In6 in pairs [figure in (10)]. Two decorations or "warts" fill out the remaining In bonding on the cage surfaces and, with Na and In₁₀Ni (B), separate the layers. As seen near the middle of Fig. 2, triangles of In11 cap the polar In9 and bond to three neighboring In8, and hexagons of In10 sit above the interstices



Fig. 1. The In_{74} fullerene, which shares pentagons about the waist to generate close-packed layers. The point symmetry is D_{3h} , with the *c* axis vertical through the polar In9 atoms (30% probability ellipsoids).

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where three In_{74} join, bonding to one In1 and two In3 on each In_{74} . The open areas beyond each of these can be considered to contain outward-pointing lone pairs of electrons and Na7 (see below). The In_{74} layers stack hexagonally with an *ab* sequence so that the added In6 hexagons lie above *a* or *b* positions in the opposed layer. The shortest distance between the augmented layers is 5.4 Å.

Distinct $M_{60} = In_{48}Na_{12}$ polyhedra $(D_{3d}, \bar{3}m)$ (Fig. 3) also lie between the In_{74} layers in position *c*, consisting of portions of the above In10 and In11 features, intraand intercluster hexagons of In6, and the remaining polar pentagons in In_{74} . These are important because each M_{60} also contains a second $In_{10}Ni$ (B) cluster much like the A unit found within In_{74} . The Na7 herein lie somewhat outside the partial In sphere because Na–In distances are naturally ~0.4 Å longer. The Na7–Na7 edges are shared with six other M_{60} units to generate another close-packed layer that, on a larger scale, gives the whole structure a double hexagonal (*acbc* · · ·) sequence with M_{60} always at *c*. The atom-for-cluster (or cage) equivalent is NiAs.

These indide phases are particularly remarkable in the sizes of the cage (cluster)



Fig. 2. A general view of $Na_{96}|n_{97}Z_2$ (Z = Ni, Pd, or Pt) with only two of the $ln_{\sim 10}Z$ units that center ln_{74} and M_{60} shown (hexagonal cell, ~16.0 Å by 47.4 Å). The ln atoms in the network and isolated clusters have open and crossed ellipsoids, respectively, and Na and Ni are solid.

units that serve as the actual building blocks in the condensed product. In contrast, polyhedra of only six metal atoms perform this role in a great many condensed pnictides, chalcogenides, and halides (18). On the other hand, the so-called Frank-Kasper phases, β -B, and so forth that are built of tetrahedra, icosahedra, and the like are often represented in terms of similarly large but interpenetrating polyhedra (19). The latter serve only as geometric guides in structures with high coordination numbers and usually have little value in bonding considerations.

The positioning of Na throughout these structures is unusual, characteristic, and a key to understanding problems of disorder of $In_{10}Z$. These cations cap all pentagonal and hexagonal faces on In_{74} and M_{60} on both sides to produce two shells of Na39 and Na32 on each, respectively. (Some Na in the outer polyhedra are inner in other cages.) These three ordered shells and the vertexface duality are emphasized in Fig. 4, where double lines interconnect both cations in the inner Na39 and these to the equivalent Na member outside of In74. An important feature here is that regular Na-In and In-In type distances throughout require that Na atoms on pentagons lie somewhat inside the mean inner shells and thereby provide the principal definition of the cavities about the innermost $In_{10}Z$. Both the A and B clusters that center the In₇₄ and M₆₀ cages, respectively, contain normal Ni or Pd atoms surrounded by more or less continuous spheres of substantial electron density that lack welldefined maxima but lie at distances appropriate to Ni-In or Pd-In. We approximated these electron distributions by refining several atoms at or near maxima to produce a collection of quite two-dimensional disks tangent to the sphere with only a few virtu-



Fig. 3. The $M_{60} = In_{48}Na_{12}$ polyhedron of D_{3d} symmetry with the principal axis vertical and In as open and Na as shaded ellipsoids. The six Na–Na (open) edges about the waist and the six pentagons near the poles (In3, 6, 8) are shared with other cages.

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ally density-free areas. The total number of In atoms in clusters A and B summed to 9.86 (9) and 10.19 (9) about Ni and 9.45 (6) and 10.07 (7) around Pd, respectively (numbers in parentheses represent standard deviations in the last significant digit). The third, lowest value is associated with the largest set of ellipsoids.

There are good precedents for such cluster species. In the presence of large cations, the heavier tetregens form deltahedral species such as closo-Ge₉²⁻, -Pb₅²⁻ and *nido*-Sn₉⁴⁻ (3) that obey modified "Wade's rules," that is, with a minimum of 2n + 2electrons for skeletal bonding in n-deltahedra (20). Indium, in particular, achieves lower charged, hypoelectronic clusters In_{11}^{7-} and $In_{10}Hg^{8-}$ ($\sim D_{3h}$, 2n - 4) (12, 16) as well as $In_{10}Zn^{8-}$ ($\sim D_{4d}$, 2n) (14) and $In_{10}Z^{10-}$ ($\sim C_{3v}$, 2n; Z = Ni, Pd, or Pt) (17) with interstitial heteroatoms. The last cluster occurs in $K_{10}In_{10}Ni$ as a tetracapped trigonal prism. Partially disordered variants of these are plausible clusters in the center of $Na_{39}@In_{74}$ (D_{3h}) and $Na_{32}@M_{60}$ (D_{3d}), where they are largely constrained by the 12 closer Na atoms. As shown in Fig. 5A for the Ni(A) example, these Na positions map very well onto the electron density voids between the refined ellipsoids in all four clusters examined in 1. A large variety of orientations arise because of the symmetry conflicts between these zones of exclusion and that of the apparent $In_{10}Z$ cluster, $\sim C_{3v}$. The clusters may also be somewhat "soft" judging from the two slightly different geometries found in K10In10Ni. The situation amounts to a kind of angular or circular incommensurability.

Strong support for the nature of $In_{10}Z$ within both cavities in 1 was obtained from refinement of the more complex but lower symmetry structure of $Na_{172}In_{197}Ni_2$ (2) (11). The In_{70} cavity has only $C_{2\nu}$ (mm) symmetry, and the fewer and smaller disk-



Fig. 4. The In_{74} cage (open ellipsoids, solid bonds) plus the inner Na_{39} polyhedron (shaded ellipsoids, open links) connected to equivalent Na atoms in the outer sphere (94% ellipsoids).

like "atoms" necessary about the Ni atom show similar features with respect to the sheath of pentagon-capping Na and sum to 10.0 (2) In. An $In_{10}Ni$ model in two tilted orientations that was completely consistent with the known $In_{10}Ni^{10-}$ could be selected by recognizing the multiplicative effects of just the two mirror planes (Fig. 5B). For comparison, one cluster in $K_{10}In_{10}Ni$ is shown in Fig. 5C (17). Possible orientations of such species in both In_{74} and M_{60} (1) can be imagined on the basis of a similar pinning of the three large quadrilateral faces of $In_{10}Ni^{10-}$ by the closer Na, but distortions and the expected sixfold disorder make the model difficult to prove.

The question of charge on the two centered In₁₀Z clusters in 1 was approached on the basis of an extended-Hückel band calculation on just a single augmented In74 layer (Fig. 2) (13, 21). This calculation showed a strongly bonding valence band dominated by In 5p orbitals between -10.2and -6.3 eV, followed by three small distinct bands centered near -5.8, -5.2, and -4.5 eV, which are slightly antibonding according to a COOP (overlap-weighted population) analysis and quite flat (≤ 0.2 eV wide) relative to those farther removed [figure in (10)]. Energies within the lower two bands behave in a mirror fashion, suggesting (weak) bonding and antibonding characteristics, and the orbital vectors show that these states arise principally from the surface triangles (In11), hexagons (In10), and In3,8 atoms near the poles in In74 that interconnect them. As expected from earlier work (13, 15), the three small bands are largely combinations of outward-pointing electron pairs on these atoms that become more antibonding with increasing energy. Placement of the Fermi energy $E_{\rm F}$ between the first two narrow bands requires 304 electrons per layer, which with 77 In atoms and 96 cations leaves a charge of -23 on the two In₁₀Ni(A,B) clusters versus -10 each in $K_{10}In_{10}Ni$. Actually, the remaining 6 electrons per cell could easily be accommodated in the third band, which is so narrow that these electrons would doubtlessly be localized. This last disposition yields a charge of -0.99 per In in the layers, virtually the same as in NaIn. The foregoing indications regarding the bonding in 1, particularly the fairly localized nonbonding electrons on the surface decorations near $E_{\rm F}$, make it unlikely that doping could readily produce a metallic, let alone a superconducting, state, in contrast to the behavior of A_3C_{60} (22). The magnetic susceptibilities of 1 are consistent with this picture (23).

Electronic and structural analogies to these new phases are provocative: NaIn is to C(diamond) as the present Na₉₆In₉₇Z₂ are to C_{60} and the other fullerenes. The electronic similarities are emphasized by the fact that 82% of the atoms in the augmented In₇₄ layers are four-bonded to other In, the rest to five or six In neighbors. The small amount of Ni, Pd, or Pt necessary to convert NaIn into this condensed fullerene structure is indeed remarkable. The interstitials may, in a very simplistic view, be associated with the creation of small, centered clusters that fill the central cavities in Na₃₉@In₇₄ and the other cages well. The bonding of Z in such well-reduced systems appears to involve principally ns and np valence orbitals, with nd^{10} states acting as inert cores (17).

These much larger, charged fullerenes are necessarily well stuffed, making the relative sizes of all the endohedral components important, as opposed to the "freestanding" C_{60} and larger examples with volumes only $\geq 9\%$ as great. Endohedral chemistry in the latter has been largely limited to a few metal atoms in La₂@C₈₀ (24), Sc₃@C₈₂ (25), and the like, although one can imagine a buckeyball chemistry developing where these are well stuffed with a variety of species.

Finally, the distinctive complexity of selected intermetallic structures, not just of In and Ga, is often a clear indication of the importance of electron-precise "valence" rules in their bonding, namely, as super Zintl phases of sorts (26). Of particular significance is Nesper's incomplete structur-



Fig. 5. (**A**) The innermost disordered cluster $In_{10}Ni$ (A) in $Na_{96}In_{97}Ni_2$ together with the positions of the closer Na atoms that cap inner pentagonal faces of the surrounding In_{74} . (**B**) The centered $In_{10}Ni$ cluster resolved within $Na_{37}@In_{70}$ in $Na_{172}In_{197}Ni_2$ (**2**) (11). (**C**) One $In_{10}Ni^{10-}$ cluster in $K_{10}In_{10}Ni$ ($\sim C_{3v}$, axis vertical) (17) (94, 50, 94% ellipsoids).

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al study of "LiMgAl₂" in which Al₇₆ (C_{3v}) superballs are condensed through all pentagonal faces to generate a well-defined ~cubic close-packed array. Additional features were evident for each sphere: surfacebonded atoms, an inner sphere (or two) of mixed cations that cap all faces of Al₇₆, and small centered Al polyhedron; however, most could not be well defined (26, 27).

There remains much to be discovered and understood about polar intermetallic systems that incorporate highly reduced main-group p metals. We expect that the structural and bonding features and principles revealed here will be important in other intermetallic structures involving main-group-element polyanions.

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- Very sharp diffraction data from bar-like $Na_{96}Ni_2$ and gem-like $Na_{96}In_{97}Pd_2$ crystals were collected at room temperature to $2\theta = 50^{\circ}$ (θ is the diffraction 9 angle) on CAD4 and Siemens/RA diffractometers, respectively. Space group P63/mmc was selected for Na₉₆In₉₇Ni₂ according to systematic absences and the intensity distribution, and the Laue class was confirmed by a film study of Na₃₆In₉₇Pd₂. Absorption effects were corrected with the aid of multiple ψ scans. Direct methods gave eleven In positions, and subsequent refinement and synthesis steps located all Ni and Na atoms. Diffuse peaks around Ni were refined as five independent In about A and three about B to yield $R(F)/R_w = 4.5/5.2\%$ [39 atoms, 229 variables, 1737 unique data ($l \ge 3\sigma_i$)]. Values of B_{iso} (isotropic temperature factor) were 4 to 19 Å² for the diffuse and 0.8 to 4.1 Å² for the normal positions. The refined composition is Na₉₆-In_{97.0(1)}Ni₂. Refinement starting with the well-behaved positions found above produced a similar distribution about Pd, and a like treatment with four In about each resulted in $R/R_w = 3.2/3.1\%$ (1896 data). The refined composition is $Na_{96}I_{96.5(1)}Pd_2$. The problematic atoms were largely unchanged in both P21/m and P2.
- Tables of atom coordinates, anisotropic displacement parameters, distances, and two additional figures for 1, Z = Ni, Pd, and a stereoview of Ni@ln₁₀@Na₃₇@ln₇₀ in 2 have been deposited. See National Auxiliary Publications Services document No. 05060 for ten pages of supplementary material. Order from American Society for Information Science–National Auxiliary Publications, Post Office Box 3513, Grand Central Station, New York, NY

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- Substantially temperature-independent (±20%) 23. susceptibilities lay between -2.6 and -1.2 (×10⁻³ electromagnetic units per mole) for the

Crystal Structure of the Polymer Electrolyte Poly(ethylene oxide)₃:LiCF₃SO₃

P. Lightfoot, M. A. Mehta, P. G. Bruce*

lonically conducting polymers (polymer electrolytes) are under intensive investigation because they form the basis of all solid-state lithium batteries, fuel cells, and electrochromic display devices, as well as being highly novel electrolytes. Little is known about the structures of the many crystalline complexes that form between poly(ethylene oxide) and a wide range of salts. The crystal structure is reported of the archetypal polymer electrolyte poly(ethylene oxide)₃:LiCF₃SO₃, which has been determined from powder x-ray diffraction data. The poly(ethylene oxide) (PEO) chain adopts a helical conformation parallel to the crystallographic b axis. The Li⁺ cation is coordinated by five oxygen atoms-three ether oxygens and one from each of two adjacent CF₃SO₃⁻ groups. Each CF₃SO₃⁻ in turn bridges two Li⁺ ions to form chains running parallel to and intertwined with the PEO chain. There are no interchain links between PEO chains, and the electrolyte can be regarded as an infinite columnar coordination complex.

Polymer electrolytes consist of salts, such as LiClO₄, that are dissolved in coordinating polymers, such as poly(ethylene oxide) $[(CH_2CH_2O)_n]$. They can exhibit ionic conductivities approaching that of many liquid electrolytes. Discovered in 1973 by Wright and co-workers (1), their potential as completely novel electrolytes with a solid solvent was recognized in 1978 by Armand and co-workers (2), who have extensively developed and exploited them. The ability to prepare polymer electrolytes in the form of thin (3 to $30 \,\mu$ m) flexible films of infinite length and with a high ionic conductivity has resulted in the development of a new generation of electrochemical devices with a solid electrolyte and solid electrodes (3). Such all-solid-state cells have a number of advantages; they can be fabricated in a wide variety of shapes, the leakage of corrosive liquids is eliminated, and complete devices can be made by automated film processing. Among the devices under development are electrochromic displays, "smart" windows, and rechargeable lithium batteries. The last

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of these can store large quantities of energy per unit weight and volume. Major investment in the United States, Europe, and Japan is targeted at the development of such batteries for electric vehicle and conthree examples. No superconductivity was evident at 100 Oe and ≥1.4 K.

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sumer electronic applications (4).

Progress in the field of polymer electrolytes has been severely restricted by the lack of structural data. Part of the difficulty is determining the crystal structures of polymer:salt complexes by single-crystal methods (5, 6). We have established the crystal structure of PEO3:NaClO4 (7) from highresolution powder x-ray data. The archetypal polymer electrolyte, LiCF₃SO₃ dissolved in poly(ethylene oxide), is the most widely investigated system, both for technological applications and fundamental studies. Here we report the elucidation of the crystal structure of the important PEO₃:LiCF₃SO₃ complex from powder x-ray diffraction data (8). The use of lowtemperature data was critical to the development of a stable structural model through Rietveld refinement. The increase in quality of the high-angle data due to the lowering of thermal motion in such a "soft" molecular system is a significant factor when studying such systems.

Initial indexing of the room-temperature data was carried out with the program

Table 1. Refined atomic parameters for PEO₃:LiCF₃SO₃ at 298 K, space group $P2_1/a$, a = 16.768(2)Å, b = 8.613(1) Å, c = 10.070(1) Å, and $\beta = 121.02(1)^\circ$. Hydrogen atoms were included in the refinement but are not reported

Atom	X	У	Z	U _{iso} * (Ų)
O(1)	0.206(2)	0.110(3)	0.090(3)	0.026(7)
C(1)	0.262(2)	0.091(3)	0.253(3)	0.026(7)
C(2)	0.366(2)	0.099(2)	0.298(2)	0.026(7)
O(2)	0.386(1)	0.246(2)	0.265(2)	0.026(7)
C(3)	0.486(1)	0.261(3)	0.341(3)	0.026(7)
C(4)	0.513(1)	0.426(3)	0.314(2)	0.026(7)
O(3)	0.455(1)	0.469(2)	0.158(2)	0.026(7)
C(5)	0.450(2)	0.631(2)	0.131(3)	0.026(7)
C(6)	0.387(2)	0.651(3)	-0.051(4)	0.026(7)
S(1)	0.2697(7)	0.124(2)	0.809(1)	0.084(9)
C(7)	0.328(1)	0.077(2)	0.703(2)	0.084(9)
O(4)	0.277(2)	-0.001(2)	0.903(2)	0.11(1)
O(5)	0.303(2)	0.264(2)	0.893(3)	0.11(1)
O(6)	0.172(1)	0.150(4)	0.693(2)	0.11(1)
F(1)	0.321(2)	0.204(2)	0.624(3)	0.24(1)
F(2)	0.284(2)	-0.031(2)	0.601(3)	0.24(1)
F(3)	0.413(1)	0.041(3)	0.798(2)	0.24(1)
Li(1)	0.156(5)	0.903(11)	0.906(9)	0.05

*Values constrained according to atom type. Li not refined.

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