The isolable matryoshka nesting doll icosahedral cluster $[As@Ni_{12}@As_{20}]^{3-}$ as a "superatom": analogy with the jellium cluster Al_{13}^{-} generated in the gas phase by laser vaporization†

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The valence electrons in the recently reported icosahedral cluster $[As@Ni_{12}@As_{20}]^{3-}$ with a Russian matryoshka nesting doll structure can be partitioned so that the central As atom has the rare gas configuration, as As^{3-}, and the intermediate Ni_{12} icosahedron receives 40 electrons from the lone pairs of the outer As_{20} dodecahedron to be isoelectronic with the Al_{13}^{-} jellium cluster found in molecular beam experiments.

One of the exciting recent developments of metal cluster chemistry has been the recognition of certain bare spherical free-electron metal clusters as "superatoms" having discrete electronic energy levels based on the so-called jellium model.[1] However, whereas in an atom the positive charge of a nucleus is concentrated at a central point, in a cluster the positive charge can be assumed to be distributed over a positive ion core of the size of the cluster. This difference is important since it leads to different closed shell electronic configurations in atoms and in jellium clusters.[1] Thus the closed shell atomic electron configurations occur at 2, 10, 18, 36, 54, and 86 electrons, corresponding to the atomic numbers of the noble gases. However, in a jellium cluster, the closed shell stable electronic configurations occur at 2, 8, 20, 40, 70, 112, and 168 electrons.[1]

Spherical jellium metal clusters have been generated in the gas phase by laser vaporization and characterized by mass spectroscopy. One of the most interesting of such clusters is Al_{13}^{-}, which has the jellium closed shell configuration of 40 electrons for $L \leqslant 3$, namely 39 electrons from the 13 aluminium atoms ($39 = 3 \times 13$) and the 40th electron from the negative charge.[2] Thus Al_{13}^{-} functions like a "superhalide" ion. Furthermore, the isoelectronic neutral species[3] CAl_{12} functions as a "supernoble gas". The closed shell of CAl_{12} is indicated by a gap of approximately 1.9 eV.[4]

An interesting question is whether such jellium spherical electronic behavior can be found in a stable metal cluster isolable in the condensed phase. An interesting candidate is the recently discovered[5] $[As@Ni_{12}@As_{20}]^{3-}$ cluster, isolated as its n-Bu_4P^+ salt and structurally characterized by X-ray diffraction. This cluster has full icosahedral symmetry (I_h) and a layer structure analogous to a Russian matryoshka nesting doll (Fig. 1).

The outer layer of $[As@Ni_{12}@As_{20}]^{3-}$ (purple in Fig. 1) consists of a regular As_{20} dodecahedron. Removing this outer As_{20} dodecahedron next gives a Ni_{12} icosahedron (blue in Fig. 1). Removal of this Ni_{12} icosahedron leaves behind only a single central arsenic atom. The available electrons in this cluster can be allocated among the layers to give each layer a closed shell electronic configuration.

Consider first the central arsenic atom. Applying the −3 overall charge of the ion to this central arsenic atom gives the As^{3-} anion, which has the stable electronic configuration of the next noble gas, namely krypton. Next, consider the outer As_{20} dodecahedral shell, which has a total of $20 \times 5 = 100$ valence electrons. These 100 electrons are partitioned into the 60 electrons required for two-center two-electron (2c–2e) bonds along each of the 30 edges of the regular dodecahedron and the 40 electrons required for a lone pair on each of the 20 arsenic atoms. Extended Hückel calculations, by the discoverers of the $[As@Ni_{12}@As_{20}]^{3-}$ cluster,[5] indicate negligible interactions between the molecular orbitals defining the As–As bonds in the outer As_{20} dodecahedron and the molecular orbitals in the inner $As@Ni_{12}$ fragment.

Finally, consider the intermediate Ni_{12} icosahedron layer. Bare nickel atoms in clusters are zero electron donors since they have filled d^{10} shells and in that sense function as pseudonoble gases.[6] However, the Ni_{12} icosahedron is well positioned to receive the

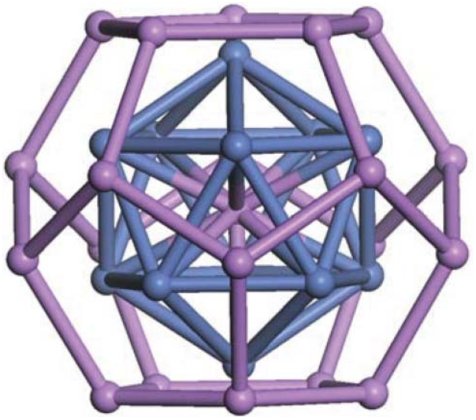

Fig. 1 Equilibrium structure of the $[As@Ni_{12}@As_{20}]^{3-}$ ion with I_h symmetry. The outer As_{20} dodecahedron and the central As atom are shown in purple whereas the intermediate Ni_{12} icosahedron is shown in blue. For clarity the connections between the Ni and outer As atoms are not indicated.

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40 electrons from the 20 lone pairs of the arsenic atoms in the outer As_{20} dodecahedron because of the dual relationship between the As_{20} dodecahedral and Ni_{12} icosahedral layers in the matryoshka nesting doll structure. Thus the overlap between these layers generates 20 tetrahedral $AsNi_3$ cavities, each of which can be the location of a 4c–2e bond. The ability of external lone pairs to function in skeletal bonding is clearly indicated in certain hypoelectronic bare clusters of the Group 13 metals,[7] notably the eleven vertex clusters E_{11}^{7-} (E = Ga, In, Tl) found in intermetallics with alkali metals.[8] Furthermore, the extended Hückel calculations of Eichhorn and co-workers[5] indicate that the 20 lone pairs on the outer As_{20} dodecahedron interact with the corresponding 20 virtual $Ni_{12}(\mu_{12}\text{-}As)^{3-}$ molecular orbitals (MOs) of the same symmetry ($a_g + t_{1u} + t_{2u} + g_u + g_g + h_g$) to give 20 bonding MOs. This is in accord with a previous[9] density functional theory (DFT) calculation on $[As@Ni_{12}@As_{20}]^{3-}$, which indicates that the binding energy between the inner $[As@Ni_{12}]^{3-}$ unit and the outer As_{20} dodecahedron is substantial, *i.e.*, about 28.2 eV.

In this chemical bonding model for $[As@Ni_{12}@As_{20}]^{3-}$, the outer As_{20} dodecahedron is seen to use its 20 "lone" electron pairs to function as an "icosadentate" ligand to the next layer, namely the Ni_{12} icosahedron. In this way the Ni_{12} icosahedron attains the stable 40 electron jellium configuration. This is also related to the structure of the known Al_{13}^{-} cluster, which is also assumed to be a centered icosahedron, although no real structural proof is yet available for this and other experimentally obtained similar gas phase species.

The matryoshka nesting doll structure of $[As@Ni_{12}@As_{20}]^{3-}$ is seen to protect components that are not stable in the free state. Thus the $As@Ni_{12}$ "stuffing" of the outer As_{20} dodecahedron prevents the dodecahedron from collapsing into more stable smaller polyhedra such as As_4, which is stabilized by spherical aromaticity.[10] Furthermore, the As_{20} outer layer stabilizes the Ni_{12} icosahedron by filling the external Ni_{12} orbitals with the As_{20} lone pairs. Finally, the central As^{3-} unit has too high a charge density to be stable in the isolated state.

Other models for the chemical bonding in $[As@Ni_{12}@As_{20}]^{3-}$ were all found to have flaws. In all cases the 60 electrons required for the 30 2c–2e edge bonds in the outer As_{20} dodecahedron were isolated from the remaining 168 of the 228 total valence electrons in the structure in accord with the original extended Hückel calculations.[5] However, the Wade–Mingos rules[11] require 170 cluster valence electrons for an icosahedral $Ni_{12}(\mu_{12}\text{-}As)$ cluster, namely 120 for the 12 filled nickel d^{10} shells, 24 for the 12 external nickel orbitals, and 26 for the skeletal icosahedral bonding ($2n + 2 = 26$ for $n = 12$ by the Wade–Mingos rules). Eichhorn and co-workers[5] account for this discrepancy by a frontier orbital energy inversion where the HOMO is a four-fold degenerate g_g MO and the LUMO is a five-fold degenerate h_g MO rather than *vice versa*. Our density functional calculations agree with them in this connection.

It is also of interest that a configuration of 168 electrons is the stable jellium sphere electronic configuration for $L \leqslant 6$.[1] However, the irreducible representations of the bonding molecular orbitals in the outer As_{20} dodecahedron and the complete $[As@Ni_{12}@As_{20}]^{3-}$ matryoshka nesting doll (see supporting information†) do not agree with the required breakdown of the 114 bonding orbitals for the 228 total valence electrons. In particular, our molecular orbital calculations using density functional theory (see supporting information†) gave four bonding non-degenerate totally symmetric a_g molecular orbitals whereas a combination of the 30 2c–2e edge bonds in the outer As_{20} dodecahedron and the components of the 84 levels for the 168 jellium sphere electrons up to $L \leqslant 6$ require six a_g orbitals.

The analysis of the chemical bonding in $[As@Ni_{12}@As_{20}]^{3-}$ outlined in this communication suggests some previously unrecognized principles governing the stability of large spherical metal clusters that go beyond the now familiar Wade–Mingos rules.[11] Thus, structural units that are potentially chemically reactive can be protected by embedding them into a matryoshka nesting doll structure related to the stabilization of unusual M_3N metal nitride moieties inside endohedral fullerenes.[12] Furthermore, this principle can be used to stabilize a jellium metal cluster sphere, namely a Ni_{12} icosahedron in $[As@Ni_{12}@As_{20}]^{3-}$. This suggests that the Al_{13}^{-} jellium sphere, currently known only in the gas phase, might be stabilized as an isolable condensed phase molecule in a matryoshka nesting doll structure, possibly even using the As_{20} dodecahedron found in $[As@Ni_{12}@As_{20}]^{3-}$ as an outer layer. In this connection, central Al_{13} units are found in the giant $[Al_{69}\{N(SiMe_3)_2\}_{18}]^{3-}$ and $[Al_{77}\{N(SiMe_3)_2\}_{20}]^{2-}$ clusters isolated by Schnöckel and co-workers[13] as etherates of their lithium salts and characterized structurally by X-ray diffraction.

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