Dalton Transactions

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Journal Name

RSCPublishing

ARTICLE

Peeling the onion: a revised model on the electron count for matryoshka clusters†‡

Cite this: DOI: 10.1039/x0xx00000x

Fu Kit Sheong, Wen-Jie Chen, Hwon Kim and Zhenyang Lin*

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

We have provided a model for understanding two isoelectronic matryoshka clusters, $[Sn@Cu_{12}@Sn_{20}]^{12-}$ and $[As@Ni_{12}@As_{20}]^{3-}$. By dividing each of the clusters in a layer-by-layer manner and allowing each layer to follow a simple electron-filling rule, we can formulate a consistent model to explain experimental and computed properties of both matryoshka clusters that cannot be adequately explained by existing models. By analysing these clusters in a way analogous to peeling an onion, we can not only have an understanding on the structure and bonding of the two matryoshka clusters under study, but also have a generalizable model to handle certain p/d-block@d-block endohedral clusters.

Introduction

Cluster chemistry has long been thought as a theoretical foundation of heterogeneous catalysis, because a lot of such catalytic pathways are believed to be related to the local microscopic structures of their catalysts, and therefore clusters were thought to be applicable to systematically study or improve heterogeneous catalysts due to their well-defined microscopic structures. At the same time, the high resemblance of some clusters to atoms, including observations like "magic numbers" which are analogous to the electronic shell structures of atoms,[1] made them also an interesting subject for theoretical studies for both chemistry and physics. Because of the potential importance in both experimental and theoretical studies, over the years the synthetic techniques for clusters have vastly improved and researchers have made numerous kinds of atomic clusters with different properties. Nowadays, clusters no longer consist of only a single element nor can only be observed by mass spectroscopic methods,[2,3] but many other examples arise that are much more stable and with more complex structures and compositions.[4–6]

Among the various types of clusters that differ in size and shape, we turn our attention to a certain group of clusters that has high symmetry with apparent shell structures, which we believe can give us a lot of theoretical insight due to their resemblance to atoms. In particular, we would like to focus on some so-called "endohedral clusters", which are clusters that have certain atoms forming a cage-like structure, with an interstitial atom lying inside the cage. In this work, we will study an extreme case of which, known as "matryoshka clusters"[7,8] or "onion-skin clusters".[9] This class of clusters is basically "endohedral cluster of endohedral cluster",[8–14] that is, instead of having an atom inside a cage, it has a cage inside a cage. Their unique structures and properties have already given rise to a number of theoretical and computational studies,[15–19] yet we still feel that our understanding to this type of clusters still resembles "a riddle, wrapped in a mystery, inside an enigma". Even though we admit that some theories or analysis did crack open the shell of the enigma, any further details on this type of clusters still remain a mystery and we believe a simple bonding picture that can serve as a key to understand their unique structures is still lacking. Therefore, in this work dedicated to the memory of Professor Wade, we would like to try to follow his insightful work on the relationship between electron counts and chemical structures, and develop a generalizable electron counting model to explain the observations we have for these matryoshka clusters and some other related endohedral clusters.

In this work, we will focus on the relationship between structure and electron count for two examples of matryoshka clusters, namely $[Sn@Cu_{12}@Sn_{20}]^{12-}$ [10] and $[As@Ni_{12}@As_{20}]^{3-}$.[9] We will try to peel these onions into layers to give a simple understanding on the electronic structures of such systems. On the way to construct a unified picture for the matryoshka clusters, we will build part of our model based on some relevant endohedral clusters.[20,21] These relevant examples have a larger variety than matryoshka clusters, indicating that the theoretical basis we found for matryoshka clusters actually has a wider applicability than the limited examples we study here.

Results and discussion

Before we start, we will first have a quick look on the two matryoshka clusters under study. On the first glance, one can

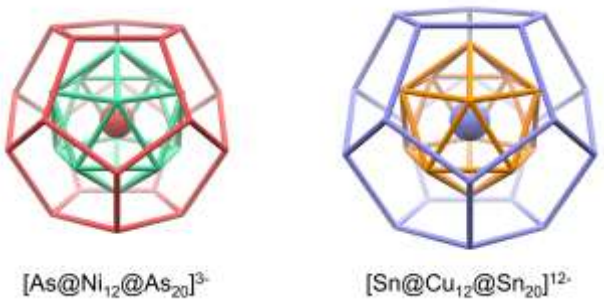


Fig. 1 Structures for the two matryoshka clusters under study. The innermost atom, icosahedron, and dodecahedron represent the core atom, the middle layer, and the outer layer, respectively. The polyhedra are drawn purely for showing the layered structure, face-dual relationship and relative sizes of matryoshka clusters, and do not imply any bonding model at this point. This and all other colour figures presented in this work are prepared by MayaVi[22] and Blender[23].

easily notice that the geometric structures of the two matryoshka clusters are essentially the same, in the sense that they can be decomposed into concentric layers of $A@B_{12}@A_{20}$ (and so they are called "matryoshka"). For the ease of discussion in the text, we will call the innermost atom A as the "core atom" or simply the "core", the B_{12} layer as the "middle layer", and the A_{20} shell on the outside as the "outer layer". It might sound redundant in the first place, but it actually gives a very important insight for the formulation of our model presented in this work. Yet before we start elaborating on our model, we will first discuss two well-known models in cluster chemistry and their applicability to the matryoshka clusters we study here.

Wade-Mingos rule

One famous model that is closely linked to cluster chemistry is the Wade's (n+1) rule, also known later as the Wade-Mingos rule.[24–26] This rule, which originated back in 1970s and is still of widespread impact today, states that a borane-like deltahedral cluster having (n+1) bonding skeletal pairs will form *closo*-structure. For clusters involving transition metals, this rule is usually generalized that 10 more electrons are added per transition metal centre. Note that if we want to apply this rule to the two matryoshka clusters shown in Fig. 1, we should first notice that the only deltahedral layer is the middle layer. Thus, the electron counting should be based on the middle layer and the core atom enclosed inside. In either cluster, we would expect that the core and the middle layer should have in total 170 valence electrons (13 skeletal pairs of electrons from (n+1) rule, 12 lone pairs of electrons where each atom contributes one lone pair, and 120 d electrons for the (n+1) rule extended for transition metal centres). However, the numbers of valence electrons from the atoms in the core and the middle layer are in total 136 (= 4 + 11×12) for $[Sn@Cu_{12}]$ and 125 (= 5 + 10× 12) for $[As@Ni_{12}]$, both of which are far from the 170 electrons required, and more than 30 electrons have to be donated from the outer shell in order to fulfil the rule. The large deviation from the (n+1) rule for the observed structures indicates that a more intuitive model beyond the Wade-Mingos rule could be developed for the two matryoshka clusters we are studying in this work.

Jellium model

Another well-known model in the field of cluster study is the jellium model,[2] which had significant impact in the 1990s, as mostly known by its early success for simple metal clusters. It was observed that total valence electron count of these clusters follows what was known as "magic numbers", and the jellium model states that these specific numbers of electrons to a large extent resemble the closing of "atomic electronic shells" and thus these clusters can be considered as "superatoms". If we attempt to apply the jellium model explanation to the two matryoshka clusters, we should expect that either the whole matryoshka cluster or the inner two layers can attain an electron count appearing in the sequence of 2, 8, 18, 20, 34, …,[1] which results from the closed electronic shell in the Woods-Saxton potential.[27] Indeed the total number of valence electrons is 16 for $[Sn@Cu_{12}]$ (without counting the 10 core-like d electrons on each copper atom) and 5 for $[As@Ni_{12}]$, so a jellium compatible charge assignment can be $[Sn@Cu_{12}]^{2-}$ (or $[Sn@Cu_{12}]^{4-}$ as argued in some work[16]), and $[As@Ni_{12}]^{3-}$. In a theoretical work by King and Zhao,[7] it was stated that the lone pair of each outer shell As in $[As@Ni_{12}@As_{20}]^{3-}$ (capping each triangular face of the icosahedral middle layer in a μ^3 manner shown in Fig. 2) donates to the middle layer, and when counted together with the valence electrons on the core atom and the d electrons on the middle layer, the cluster attains the 168 electron jellium configuration. In a more recent work by the same research group, Zhao *et. al.* has applied a similar rule to predict the existence of $Sn@Mn_{12}@Sn_{20}$ and several other

Fig. 2 A schematic representation based on the jellium model as described by King and Zhao.[7] Taking $[As@Ni_{12}@As_{20}]^{3-}$ as an example, the core (red sphere) has 5 valence electron, the Ni_{12} middle layer (green icosahedron) has 120 d electrons, and the "lone pair" from each As from the outer layer (20 pairs in total) donates to the icosahedron in a μ^3 manner (pink rods, which when taken together with the icosahedron forms a great stellated dodecahedron). Summing up all these with the three overall negative charges of the cluster, gives a total of 168 (= 5 + 120 + 40 + 3), which is one of the "magic number" in the jellium model. The same counting can also be applied to $[Sn@Cu_{12}@Sn_{20}]^{12-}$.

matryoshka clusters.[28]

Up till now, it does sound that the jellium model can serve as a simple and intuitive model for the two matryoshka clusters under study. Indeed if we treat the whole cluster as a black box and try to figure out the total charge of the cluster, the jellium model might already be adequate. Yet at the same time because the jellium model only considers the total electron count of a cluster without taking into account the constituents of the cluster in detail, we think that it only cracks open the shell of the enigma, while the more detailed bonding information within the cluster will still remain as the riddle wrapped in a mystery. We have therefore carried out density functional theory (DFT) calculations followed by Natural Population Analysis (NPA) to try to dig out the missing details from the jellium model prediction and provide a simple yet insightful understanding of the structure and bonding in the two matryoshka clusters.

As seen in Table 1, NPA indicates that the core receives electrons to become negatively charged in both matryoshka clusters, consistent with the view presented above based on the jellium model. On the other hand, as seen in our previous discussion, the jellium model argues that the electron donation was made by the outer shell, indicating that atoms on the outer shell should have net positive charge. However, this is not the case in NPA of either matryoshka cluster, which predicts a negatively charged outer shell. Thus, the NPA result cannot provide support to the jellium model, which might either due to the highly delocalized nature of jellium model (as seen by its other name as "uniform electron gas"), or due to the its intrinsic inadequacy. In any case, we believe that a more comprehensive and intuitive localized model can be made on this system, and such localization can give us a more modular picture that allows us to construct other clusters by putting more atoms together.

Table 1 Average charges on atoms for different layers of matryoshka clusters from Natural Population Analysis (NPA).

Clusters	Natural charge	
$[As@Ni_{12}@As_{20}]^{3-}$	As (Core)	-0.714
	Ni	0.096
	As (Outer)	-0.172
$K_{12}[Sn@Cu_{12}@Sn_{20}]$	Sn (Core)	-2.444
	Cu	0.623
	Sn (Outer)	-0.837
	K	0.976

Our model

As said before, the most important feature of the matryoshka clusters is that they can be decomposed into layers. Therefore, an intuitive model is to understand the clusters in a layer-by-layer manner. As said in the title, we will try to dissect each of the clusters as if we were peeling an onion, and understand the clusters in an outside-in manner.

To begin with, we will first pay attention to the fact that the outer layers of the two matryoshka clusters are both in the shape of a regular dodecahedron. One might immediately notice that this is a 3-connected polyhedron, and thus each outer layer resembles an "electron precise" polyhedral cluster in Mingos' Polyhedral Skeletal Electron Pair Theory (PSEPT).[25] This implies that the total number of valence electrons for the whole cluster should be 5n, or in other words all main group atoms which build up the cluster should simply follow the octet rule. Because of this, we would expect each atom should be assigned with a valence electron count of 5, thus in the $[As@Ni_{12}@As_{20}]^{3-}$ cluster, the As_{20} layer should be stable with neutral charge. This prediction has actually been computationally verified and discussed in various work in the literature.[29–31] On the other hand, in the cluster of $[Sn@Cu_{12}@Sn_{20}]^{12-}$, because Sn is in group 14 and has only 4 valence electrons, if we make an analogy from As_{20}, we would expect a charge of 1- on each of the Sn atoms on Sn_{20}, giving a total charge of 20- on the outer layer of the cluster. In other words, to follow the octet rule, the outside layer consists of a 3-connected cluster of $[Sn_{20}]^{20-}$.

With the outside layer of the onion properly peeled off, we will move on to the handling of the middle layer and the core. The middle layer in each of the two matryoshka clusters resembles an icosahedron, which falls into the group of *closo*-deltahedra. As discussed before, one intuitive move is to apply the (n+1) rule, but actually due to the relatively poor availability of the p orbitals (from the middle layer atoms) for bonding,[32] the Wade's (n+1) rule is not the most appropriate choice.

Here, instead of directly providing an argument, we would first put forward several examples from the literature that feature a p-block@d-block type of endohedral clusters,[20,21] in which the p orbitals of the d-block elements are not fully available for bonding, and start to formulate a general rule from them.

To begin with, we will start with two examples of endohedral gold clusters, $[(Ph_3PAu)_4N]^+$,[33] and $[(Ph_3PAu)_5N]^{2+}$.[34] From Wade's (n+1) rule extended for d-block elements, they should have valence electron counts of 58 (10 bonding skeletal electrons, 40 d electrons and 8 electrons for the 4 metal-phospine σ bonds) and 72 (12 bonding skeletal electrons, 50 d electrons and 10 electrons for the 5 metal-phosphine σ bonds) respectively. Note that the valence electron counts of these two clusters are 56 (= 11×4 + 5 + 8 - 1) and 68 (= 11×5 + 5 + 10 - 2) respectively, which are clearly less than those predicted by Wade's rule. At the same time, 56 and 68 cannot both fall into the list of magic numbers, indicating that the jellium model cannot be used to consistently explain the stability of these clusters either.

To seek for a reasonable explanation, we first note that these two clusters differ only by an $AuPPh_3$ unit. From the fact that the numbers of their electron counts differ by 10, and PPh_3 is neutral in charge, we can assign a d^{10} electron count for each Au centre. If we believe that this observation is transferrable to all Au centres, we can assign all Au centres to an electron configuration of d^{10} and each $AuPPh_3$ unit to a net charge of 1+. By summing up all these d electrons contributed by all the Au centres, we have a total of 40 for $[(Ph_3PAu)_4N]^+$, and 50 for $[(Ph_3PAu)_5N]^{2+}$. Given that the numbers of valence electrons

are 48 and 58 respectively, we know that the interstitial nitrogen should take the remaining 8 electrons (thus having a charge of 3-) and so by itself attain a stable octet.

In this way, we can handle the two p-block@d-block endohedral clusters by first peeling off a layer of d^{10} centres, and then assign the remaining core to have an octet configuration. One might argue that this is merely a coincidence, yet a quick search on the literature can give examples with different core atoms and different number of ligands (Fig. 3), of which a simple comparison can give us an idea of how far our model can go.

For example, we can compare different core atoms across the period. We can see from the literature that for endohedral gold clusters in the form of $[(R_3PAu)_4X]^{n+}$, we have examples like $\{[(c\text{-}C_6H_{11})_3PAu]_4C\}$,[35] $[(Ph_3PAu)_4N]^+$,[33] or $\{[(o\text{-tolyl})_3PAu]_4O\}^{2+}$.[36] If we take each $AuPR_3$ unit with a net charge of 1+ by assigning Au to an electron configuration of d^{10}, and fill each interstitial atom with enough electrons to attain octet (so that C has a charge of 4-, N has 3-, O has 2-), we can see that the sum of total charges of each cluster is consistent with the experimental observations.

If we wish to continue our comparison on clusters with different number of ligands, we can have multiple examples of endohedral clusters with a carbon centre, in particular, there are $\{[(c\text{-}C_6H_{11})_3PAu]_4C\}$,[35] $[(Ph_3PAu)_5C]^+$,[37] and $[(Ph_3PAu)_6C]^{2+}$,[38] which feature a carbon staying inside an Au_n cage with n = 4, 5, and 6, respectively. It can be easily seen that with introduction of each $AuPR_3$ unit, the total charge of the complex increases by 1+, consistent with the assignments we made.

If we instead wish to go down the group of the periodic table, we can see a comparison between $[(Ph_3PAu)_4N]^+$ [33] and $[(Ph_3PAu)_4As]^+$.[39] It is interesting to see that although both clusters have the same total charge (consistent with our model), they have different geometries. $[(Ph_3PAu)_4N]^+$ has the N atom lying completely inside the cage formed by the Au centres, whereas $[(Ph_3PAu)_4As]^+$ has the As atom lying on top of the square formed by Au_4. This possibility to rearrange bonding topology for the Au "cluster" indicates that classical Au-Au bonding might not be a suitable picture for the interaction between Au units. In fact in our model, Au can attain an electron count of 14 valence electrons for a linear coordination, and no "classical" bonds were formed between Au atoms. Thus, when the size of the endohedral atom becomes too large (by changing from N to As), the Au_4 cluster can easily change shape without breaking any classical bonds. Still, it is known that due to relativistic effect, non-classical Au(I)-Au(I) attractive interactions do exist (known as "aurophilicity"),[38,40] which can explain the reason why a lot of endohedral Au_n clusters have been observed even though from our argument no classical bonds should be present among the Au centres, and also why the Au centres stay together and form a square shape in $[(Ph_3PAu)_4As]^+$. A similar rearrangement can also be seen between S and Au_4 in $[(Ph_3PAu)_4S]^{2+}$ cluster[41] when compared with the corresponding analogue **O4** (Fig. 3).

Other gold clusters with elements like P, Se or Cl as the interstitial atom also exists,[21] and can all be properly elucidated by applying the rule we mentioned above.

Although our aforementioned discussions are all focused on p-block@d-block type of endohedral clusters, it can actually be applied also to the d-block@d-block type of endohedral clusters with a simple twist: instead of assigning an octet structure for the core atom, we can assign the number of valence electrons to the centre atom according to the coordination geometry (18 in most cases, unless we come across oblate (16) or prolate (14) clusters[42]). A quick glance through the literature can give us a long list of such d-block@d-block clusters,[43] many of which are of icosahedral shape. If we take $[W@Au_{12}]$ and $[Au@Au_{12}(PMe_2Ph)_{10}Cl_2]^{3+}$ as examples,[44–46] it can be easily seen that if we assign each Au unit on the outer shell to have a charge of 1+, and fill up enough electrons for the core atom to attain the 18 electron rule (12 additional electrons for W, and 7 for Au), the total charge as predicted from our model matches well with the experimental observations. A very recently reported Ag cluster,[47] $[Ag_{21}\{S_2P(OiPr)_2\}_{12}]^+$, can also effectively be considered as $[Ag@Ag_{12}@Ag_8\{S_2P(OiPr)_2\}_{12}]^+$ and be elucidated in a similar manner by considering all silver atoms in the middle and outer layer to have a d^{10} configuration.

Moving back to our matryoshka clusters, as we have mentioned, after peeling off the outer layer as a 3-connected cluster, we are left with an endohedral cluster with a p-block@d-block structure. We can apply our model and argue that all centres on the "middle layer" of the matryoshka cluster (which serves as the outer layer of the endohedral cluster) should each have a d^{10} electron configuration, and the core atom should have an octet configuration. This means that for the $[As@Ni_{12}@As_{20}]^{3-}$ cluster, the Ni_{12} layer is formally neutral in charge (because Ni is in group 10), where the core As atom takes three extra electron to attain octet and thus has a charge of 3-. Similarly, for the $[Sn@Cu_{12}@Sn_{20}]^{12-}$ cluster, each Cu atom on the Cu_{12} layer loses one electron to attain a d^{10}

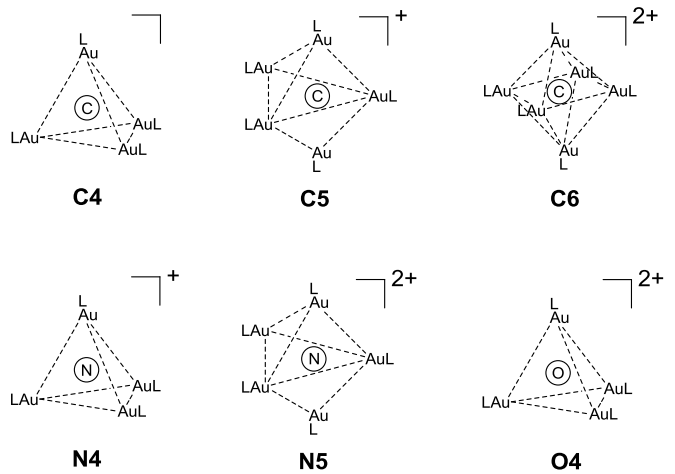


Fig. 3 Selected examples of endohedral gold clusters. Cluster with carbon centre with an Au cage with 4 Au (**C4**)[35], 5 Au (**C5**)[37], and 6 Au centres (**C6**)[38]; cluster with nitrogen centre with an Au cage with 4 Au (**N4**)[33] and 5 Au centres (**N5**)[34]; and cluster with an oxygen centre with 4 Au centres (**O4**)[36] are presented.

configuration, so we assign Cu_{12} with a charge of 12+, and the core Sn atom takes four extra electron to attain octet and has a formal charge of 4-. Here we would like to emphasize that the assignment of 4- to the core Sn is purely formal for electron counting. One thing that is certain is that the 8 electrons are shared/delocalised between the core and the middle layer, and the formal assignment of all 8 electrons to the core atom is for the convenience of assigning all atoms in the middle layer as having d^{10} configuration each.

One might consider the possible connections between the $[As@Ni_{12}@As_{20}]^{3-}$ cluster presented here and solid NiAs crystal due to their similarities in constituents. Though in the $[As@Ni_{12}@As_{20}]^{3-}$ cluster, the Ni centres in the middle layer are of d^{10} configurations, and the interactions among these Ni centres should be analogous to the d^{10}-d^{10} attractive interaction as seen in quadruple salt of silver(I)[48] (termed "argentophilicity") and in group 10 metal bulks, thus this kind of interaction is weaker than those found in NiAs crystal. In NiAs, the nickel centres are not having d^{10} configuration and the Ni-Ni distances are shorter.[49]

One final comment will be regarding the interaction between the outer layer and the middle layer. Our model does not explicitly handle the interaction between these two layers, yet this does not imply that there is no interaction between them. The outer layer by itself forms a stable 3-connected cluster and its interaction with the middle layer is like to be of van der Waals type. In any case, the interaction between the two layers should not be very strong.

Comparison with the computational results

As mentioned before, although the jellium model gives a useful prediction for the total number of valence electrons, it is inconsistent with the charge assignment with NPA. Our model, on the other hand, shows a much better agreement with the computational results. In particular, our model successfully predicted that the charge on the outer two layers of the $[As@Ni_{12}@As_{20}]^{3-}$ cluster is close to 0, and the core As has a highly negative charge. For the $[Sn@Cu_{12}@Sn_{20}]^{12-}$ cluster, we noticed significant positive charges on Cu atoms and significant negative charges on the outer Sn atoms, and the core Sn has the most negative charges among all (Table 1), consistent with the qualitative prediction of our model.

Moreover, from our proposed explanations, we expect complete 2-centre-2-electron bonds between atoms on the outer layer, while we expect minimal interactions between atoms on the middle layer. This indeed is the case from our calculations, in the sense that the highest Wiberg bond index occurs among the main group atoms on the outer layer in both cases (Table 2). The interaction between the outer layer and the middle layer is noticeable yet far less significant than the bonds among atoms on the outer layer, indicating that it might be more appropriate to explain the outer layer as a complete cage than a layer of μ^3 cap for the middle layer, with the latter explanation being used in several references.[7,50]

Table 2 Wiberg bond indices for interactions on different layers of matryoshka cluster.

Clusters	Wiberg bond indices	
$[As@Ni_{12}@As_{20}]^{3-}$	As (Core)-Ni	0.099
	Ni-Ni	0.028
	Ni-As (Outer)	0.207
	As (Outer)-As (Outer)	0.675
$K_{12}[Sn@Cu_{12}@Sn_{20}]$	Sn (Core)-Cu	0.103
	Cu-Cu	0.017
	Cu-Sn (Outer)	0.107
	Sn (Outer)-Sn (Outer)	0.780
	Sn (Outer)-K	0.017

Examining As-As and Sn-Sn bond distances, we notice that the bond lengths in the matryoshka clusters are slightly longer than the normal single bond distance (As: 2.51Å[51] versus 2.747Å; Sn: 3.06Å[52] versus 3.17Å), consistent with the smaller-than-one Wiberg bond index. The slightly longer bond lengths when compared with the normal single bond lengths can be interpreted as a result of the less dominant interactions between the outer layer and the middle layer.

Peeling hypothetical onions

As discussed in the previous sections, although Wade's rule might not be the best model for the matryoshka clusters discussed in this work because of the poor availability of the p orbitals (from the middle layer) for bonding, the overall electron counts from the jellium model might not be wrong, albeit it fails to give a detailed picture on the bonding between different units in the clusters. With this in mind, it would be interesting for us to examine some predictions based on the jellium model, and see if our model is electronically consistent and whether we can give richer details to these structure predictions. In a recent work of Zhao *et. al.*, several possible clusters were proposed based on the argument of jellium electron counts,[28] with the general formula of the list of predicted structures being $A@B_{12}@A_{20}$ (A = Sn, Pb; B = Mg, Zn, Cd, Mn). It can be seen that the two elements for A are both group 14 elements, meaning that each A on the outer layer requires one extra electron to become an electron-precise 3-connected cluster $[A_{20}]^{20-}$ according to PSEPT, and the core A needs 4 extra electrons to become the octet A^{4-}, both of these are analogous to the analysis in the $[Sn@Cu_{12}@Sn_{20}]^{12-}$ cluster. On the other hand, the potential candidates of B have group 2, group 7 and group 12 elements. Consider that if each B gives out 2 valance electrons, these B centres will each attain d^0, d^5, and d^{10} electron configurations, corresponding to empty, half-filled, and full-filled d subshells, respectively, which are all known to be stable. It is then interesting to note that when each B attains a charge of 2+, the middle shell will become $[B_{12}]^{24+}$, and the total charge of 24+ will cancel out with the sum of the core atom and the outer layer, giving a neutral overall charge that is consistent with the prediction in their work.

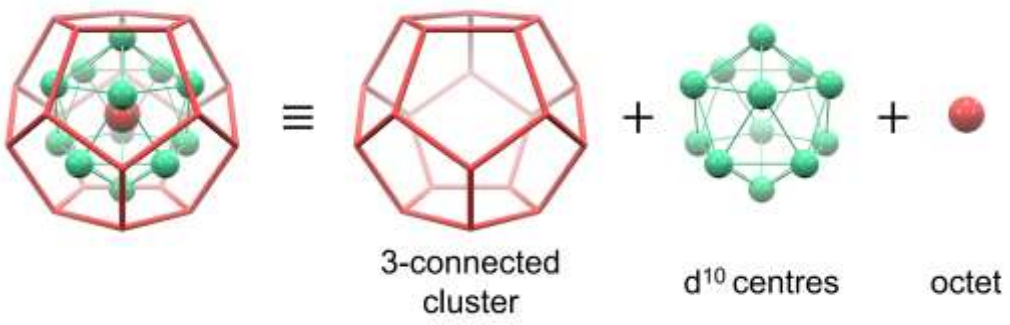


Fig. 4 Our model for understanding the matryoshka clusters. Taking $[As@Ni_{12}@As_{20}]^{3-}$ as an example, we first peel off the outer 3-connected cluster (red dodecahedron) and handle it based on the electron precise clusters (5 valence electron for each vertex), then we unwrap the middle layer of transition metal centres by making all of them to have a d^{10} electron configuration. We expect no classical bonding interactions between these d^{10} centres (green spheres), and they are held together merely by weak d^{10}-d^{10} interactions (thin green bonds). Finally we are left with a core atom (red sphere), which we will assign with an octet electronic configuration. The same peeling procedure can also be applied to $[Sn@Cu_{12}@Sn_{20}]^{12-}$, and the way to handle the core and middle layer is also applicable to certain p/d-block@d-block endohedral clusters as described in text.

Conclusions

In short, we have provided a consistent bonding model for understanding the two isoelectronic matryoshka clusters. By dividing each of the clusters in a layer-by-layer manner and allowing each layer to follow a simple electron-filling rule, we can solve this riddle wrapped in a mystery inside an enigma. We can first peel off the 3-connected outer layer and handle it as an electron precise cluster based on PSEPT, then unwrap the middle layer as a layer with each centre having a stable d^{10} configuration, leaving the core atom with an octet electronic configuration. By doing this, we can not only have an understanding on the structure and bonding of the two matryoshka clusters under study, but also have a generalizable model to handle p/d-block@d-block endohedral clusters when the p orbitals of the d-block elements on the shell are not fully available for bonding.

Computational Details

All DFT calculations are performed with the Gaussian 09 program.[53] PBE0 density functional model was chosen for all the presented calculations.[54] Due to the potential weakness for DFT to handle highly anionic species, computation for $[Sn@Cu_{12}@Sn_{20}]^{12-}$ is done based on $K_{12}[Sn@Cu_{12}@Sn_{20}]$, with all K atoms capping all the pentagonal faces of the Sn_{20} shell based on the crystal structure. All elements except K were described by the def2-TZVP basis set,[55] with the effective core potential built-in for the basis set used to describe Sn. K was described by the 6-31+G* basis set.[56] Natural population and Wiberg bond index analysis was done by NBO6.0 program based on the optimized structure.[57]

Acknowledgements

This work was supported by the Research Grants Council of Hong Kong (HKUST 603313). F.K.S. acknowledges support from the Hong Kong Ph.D. Fellowship Scheme 2012/13 (PF11-08816).

Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, People's Republic of China. *E-mail: chzlin@ust.hk*

† This work is dedicated to Professor Kenneth Wade in memory of his outstanding contribution in the bonding and structure theory of electron-deficient cluster compounds

‡ Electronic Supplementary Information (ESI) available: Cartesian coordinates of optimized structures for both matryoshka clusters, and detailed analysis results from NBO6.0. See DOI: 10.1039/b000000x/

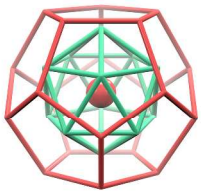
References

1 Z. Luo and A. W. Castleman, *Acc. Chem. Res.*, 2014, **47**, 2931–2940.
2 W. D. Knight, K. Clemenger, W. A. de Heer, W. A. Saunders, M. Y. Chou and M. L. Cohen, *Phys. Rev. Lett.*, 1984, **52**, 2141–2143.
3 W. D. Knight, W. A. de Heer, K. Clemenger and W. A. Saunders, *Solid State Commun.*, 1985, **53**, 445–446.
4 S. Scharfe, F. Kraus, S. Stegmaier, A. Schier and T. F. Fässler, *Angew. Chem. Int. Ed.*, 2011, **50**, 3630–3670.
5 T. F. Fässler and S. D. Hoffmann, *Angew. Chem. Int. Ed.*, 2004, **43**, 6242–6247.
6 J. D. Corbett, *Angew. Chem. Int. Ed.*, 2000, **39**, 670–690.
7 R. B. King and J. Zhao, *Chem. Commun.*, 2006, 4204–4205.
8 K. Damianos, P. Solokha and R. Ferrando, *RSC Adv.*, 2013, **3**, 9419–9430.
9 M. J. Moses, J. C. Fettinger and B. W. Eichhorn, *Science*, 2003, **300**, 778–780.
10 S. Stegmaier and T. F. Fässler, *J. Am. Chem. Soc.*, 2011, **133**, 19758–19768.

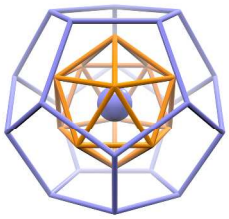
11 X.-J. Kong, L.-S. Long, R.-B. Huang, L.-S. Zheng, T. D. Harris and Z. Zheng, *Chem. Commun.*, 2009, 4354–4356.
12 J.-T. Wang, C. Chen, E. G. Wang, D.-S. Wang, H. Mizuseki and Y. Kawazoe, *Appl. Phys. Lett.*, 2009, **94**, 133102.
13 T.-S. Wang, N. Chen, J.-F. Xiang, B. Li, J.-Y. Wu, W. Xu, L. Jiang, K. Tan, C.-Y. Shu, X. Lu and C.-R. Wang, *J. Am. Chem. Soc.*, 2009, **131**, 16646–16647.
14 X.-J. Kong, Y.-P. Ren, W.-X. Chen, L.-S. Long, Z. Zheng, R.-B. Huang and L.-S. Zheng, *Angew. Chem. Int. Ed.*, 2008, **47**, 2398–2401.
15 J. Zhao and R.-H. Xie, *Chem. Phys. Lett.*, 2004, **396**, 161–166.
16 A. Muñoz-Castro, *J. Phys. Chem. Lett.*, 2013, **4**, 3363–3366.
17 T. Baruah, R. R. Zope, S. L. Richardson and M. R. Pederson, *Phys. Rev. B*, 2003, **68**, 241404.
18 T. Baruah, R. R. Zope, S. L. Richardson and M. R. Pederson, *J. Chem. Phys.*, 2004, **121**, 11007–11015.
19 H.-T. Liu and J.-M. Li, *Chin. Phys.*, 2005, **14**, 1974.
20 H. Schmidbaur and A. Schier, *Chem. Soc. Rev.*, 2011, **41**, 370–412.
21 H. Schmidbaur, *Pure Appl. Chem.*, 1993, **65**, 691–698.
22 P. Ramachandran and G. Varoquaux, *Comput. Sci. Eng.*, 2011, **13**, 40–51.
23 Blender Online Community, *Blender - a 3D modelling and rendering package*, Blender Foundation.
24 K. Wade, *J. Chem. Soc. Chem. Commun.*, 1971, 792–793.
25 D. M. P. Mingos, *Acc. Chem. Res.*, 1984, **17**, 311–319.
26 A. J. Welch, *Chem. Commun.*, 2013, **49**, 3615.
27 R. D. Woods and D. S. Saxon, *Phys. Rev.*, 1954, **95**, 577–578.
28 X. Huang, J. Zhao, Y. Su, Z. Chen and R. B. King, *Sci. Rep.*, 2014, **4**, 6915.
29 T. Baruah, M. R. Pederson, R. R. Zope and M. R. Beltrán, *Chem. Phys. Lett.*, 2004, **387**, 476–480.
30 A. J. Karttunen, M. Linnolahti and T. A. Pakkanen, *ChemPhysChem*, 2007, **8**, 2373–2378.
31 P. Nava and R. Ahlrichs, *Chem. – Eur. J.*, 2008, **14**, 4039–4045.
32 Z. Lin, R. P. F. Kanters and D. M. P. Mingos, *Inorg. Chem.*, 1991, **30**, 91–95.
33 Y. L. Slovokhotov and Y. T. Struchkov, *J. Organomet. Chem.*, 1984, **277**, 143–146.
34 A. Grohmann, J. Riede and H. Schmidbaur, *Nature*, 1990, **345**, 140–142.
35 H. Schmidbaur and O. Steigelmann, *Z. NATURFORSCHUNG B*, 1992, **47**, 1721–1721.
36 H. Schmidbaur, S. Hofreiter and M. Paul, *Nature*, 1995, **377**, 503–504.
37 F. Scherbaum, A. Grohmann, G. Müller and H. Schmidbaur, *Angew. Chem. Int. Ed. Engl.*, 1989, **28**, 463–465.
38 F. Scherbaum, A. Grohmann, B. Huber, C. Krüger and H. Schmidbaur, *Angew. Chem. Int. Ed. Engl.*, 1988, **27**, 1544–1546.
39 E. Zeller, H. Beruda, A. Kolb, P. Bissinger, J. Riede and H. Schmidbaur, *Nature*, 1991, **352**, 141–143.
40 H. Schmidbaur, *Gold Bull.*, 2000, **33**, 3–10.
41 F. Canales, C. Gimeno, A. Laguna and M. D. Villacampa, *Inorganica Chim. Acta*, 1996, **244**, 95–103.
42 Z. Lin, T. Slee and D. M. P. Mingos, *Chem. Phys.*, 1990, **142**, 321–334.
43 P. Schwerdtfeger, *Angew. Chem. Int. Ed.*, 2003, **42**, 1892–1895.
44 P. Pyykkö and N. Runeberg, *Angew. Chem. Int. Ed.*, 2002, **41**, 2174–2176.
45 X. Li, B. Kiran, J. Li, H.-J. Zhai and L.-S. Wang, *Angew. Chem. Int. Ed.*, 2002, **41**, 4786–4789.
46 C. E. Briant, B. R. C. Theobald, J. W. White, L. K. Bell, D. M. P. Mingos and A. J. Welch, *J. Chem. Soc. Chem. Commun.*, 1981, 201–202.
47 R. S. Dhayal, J.-H. Liao, Y.-C. Liu, M.-H. Chiang, S. Kahlal, J.-Y. Saillard and C. W. Liu, *Angew. Chem. Int. Ed.*, DOI: 10.1002/anie.201410332.
48 Q.-M. Wang and T. C. W. Mak, *J. Am. Chem. Soc.*, 2001, **123**, 1501–1502.
49 J. G. Thompson, A. D. Rae, R. L. Withers, T. R. Welberry and A. C. Willis, *J. Phys. C: Solid State Phys.*, 1988, **21**, 4007.
50 R. B. King, in *Zintl Ions*, ed. T. F. Fässler, Springer Berlin Heidelberg, 2011, pp. 1–24.
51 N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, Oxford University Press, 2012.
52 Y. Peng, R. C. Fischer, W. A. Merrill, J. Fischer, L. Pu, B. D. Ellis, J. C. Fettinger, R. H. Herber and P. P. Power, *Chem. Sci.*, 2010, **1**, 461–468.
53 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09 Revision D.01*.
54 C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158–6170.
55 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.
56 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213–222.
57 E. D. Glendening, C. R. Landis and F. Weinhold, *J. Comput. Chem.*, 2013, **34**, 1429–1437.

Peeling the onion: a revised model on the electron count for matryoshka clusters†‡

Fu Kit Sheong, Wen-Jie Chen, Hwon Kim and Zhenyang Lin*



$[As@Ni_{12}@As_{20}]^{3-}$



$[Sn@Cu_{12}@Sn_{20}]^{12-}$

A model for understanding two isoelectronic matryoshka clusters based on a layer-by-layer electron count assignment was presented.