Clustering Behaviour In M₈K₆ Bimetallic Clusters
(M=Li, Na, K, Rb, Cs, Mg and Al): A Density Based Molecular Dynamic Study

C. Majumder * and S. K. Kulshreshtha

Novel Materials and Structural Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400 085, India

Clustering behaviour of the constituent alkali metals, in bimetallic clusters has been investigated for M₈K₆ clusters (M=Li, K, Rb, Cs, Mg and Al) using a recently developed orbital free molecular dynamics method. For Li₈K₆ and Na₈K₆, the lithium or sodium atoms form a distorted inner cube whose six faces are capped by K atoms. In contrast, for Rb₈K₆ and Cs₈K₆, the K atoms form an inner octahedron whose faces are capped by Rb or Cs atoms. The isoatomic K₁₄ and Al₁₄ clusters form an icosahedral configuration with one of its face being capped by the fourteenth atom. For Mg₈K₆ and Al₈K₆ clusters, the Mg or Al atoms form a distorted cubic inner core of the cluster. From these results, it is inferred that for such bimetallic clusters the element with smaller atomic radius, higher electronegativity, and larger number of valence electrons, forms the core of the cluster.

(Received May 29, 2001; Accepted September 13, 2001)

Keywords: atomic cluster, bimetallic cluster, density functional theory, molecular dynamics, electronic structure

1. Introduction

The study of mixed metal clusters is of fundamental importance to understand the bonding characteristics and spatial distribution of the constituent elements. A number of physico-chemical properties of the molecules and clusters are governed by surface atom.¹-³ In contrast to the bulk, surface effects are more pronounced for smaller clusters because of large value of surface to volume ratio. Therefore, it is desirable to know the distribution of atoms in a bimetallic cluster to predict their physico-chemical properties. In earlier studies of doped bimetallic clusters for Li₈Al¹⁰ and Al₁₂Li₈,³ it was observed that for Li₈Al clusters the impurity Al atom gets trapped inside the cage formed by Li atoms for n > 6. Unlike this, the Li impurity atom is always capping one of the triangular faces formed by Al atoms from outside. For Al₈Sb⁶ clusters the Sb atom was found to have a tendency of trapping inside the Al₁₄ clusters for n > 8 and for Al₁₂Sb, the Sb atom is placed at the central position of the icosahedron. In another study of Li₈Al₁₄ clusters, it was reported⁷ that Al atoms form the core of the cluster and Li atoms are placed outside this core for n > 4. Based on these results it was inferred that the electronic character of the constituent elements plays an important role in deciding their relative distribution. Inspired by this we had investigated⁶ a large number of high symmetry A₂B₄ bimetallic clusters (A, B=Li, Na, K, Rb, Cs, Mg, Sr, Al, Si, Sb) and the following inferences were drawn: (a) The structure of heteroatomic A₂B₄ clusters is different from their corresponding isoatomic M₈ clusters. (b) All the A₂B₄ clusters attain a similar configuration i.e., an inter-penetrating tetrahedron where A type of atoms form the core tetrahedron surrounded by B type of atoms which are capping its triangular faces and form the outer tetrahedron. (c) For bimetallic clusters, the lowest energy structure is primarily governed by their atomic size, the number of valence electrons, the dimer dissociation energies and the electronegativity values of the constituent elements. To further substantiate the inferences drawn from the study of A₂B₄ clusters we have carried out similar calculations for another composition of bimetallic clusters M₈K₆, (M=Li, Na, K, Rb, Cs) consisting of fourteen atoms of alkali metals, where the constituent atoms differ in their atomic size and electronegativity values. The results have been compared with those obtained for the isoatomic monatomic K₁₄ cluster. The specific choice of this M₈K₆ cluster composition was governed by the following facts. (i) For isoatomic clusters, the thirteen-atom cluster exhibits an icosahedral structure and the fourteenth atom may either cap one of its triangular faces or the structure may completely change. (ii) The FCC unit cell contains 14 atoms placed at the centers of the six faces and vertices of the cube. For heteroatomic M₈K₆ clusters these two types of atoms may segregate out at these two different sites. (iii) The 14 atom cluster may evolve out either as an inner cube whose faces are capped by the other type of atoms, or an inner octahedral core comprised of one type of atoms whose faces are capped by the other type of atoms. Thus it is of interest to calculate the equilibrium geometry of bimetallic M₈K₆ type clusters for a variety of monovalent M atoms, so as to understand the role of electronic characteristics of M atoms in deciding the structure of such bimetallic clusters. Further to see the effect of the number of valence electrons of M atom, similar calculations have been also carried out for magnesium and aluminium atoms. In this communication we report the results obtained for the monovalent bimetallic M₈K₆ clusters and compare these results with those obtained for Mg₈K₆ and Al₈K₆ clusters where the number of valence electrons of M atoms has been varied. A comparison of these results with those reported earlier for A₂B₄ clusters,⁸ has helped us to rationalise the role of different physico-chemical characteristics of the constituent elements such as electronegativity, atomic size, the dimer bond dissociation energy and the cohesive energy, in deciding the relative distribution of the two types of atoms in bimetallic clusters.

*Corresponding author: E-mail: majumder@imr.edu. Present address: IMR, Tohoku University, Sendai 980-8577 Japan.
2. Computational Details

The ground state energetics and geometries of $M_8K_6$ bimetallic clusters have been calculated by using density functional theory based molecular dynamics simulation method. A detailed description of this method is presented elsewhere. The total energy was calculated using Hohenberg-Kohn theorem where all the energy components are described in terms of density only. The kinetic energy functional of this equation was approximated by Thomas-Fermi and Weizsacker terms, which are combined with an appropriately chosen finite correction term. The total energy of the system was minimized for fixed atomic positions using conjugate gradient method. The electron ion interaction term in the above equation was described by local norm-conserving pseudopotentials of Bachelet, Hamman and Schulter. For exchange-correlation interaction energy, the Ceperley-Alder form as parametrised by Pedrew and Zunger was used.

The geometry optimisation for all $M_8K_6$ clusters was carried out using molecular dynamics simulation method. The simulations were done by placing the cluster inside a periodically repeated unit cell of length 35 a.u. divided into a $64 \times 64 \times 64$ cubic mesh. Plane wave expansion was used on the entire fast Fourier transform mesh with an energy cutoff of 95 Ry. A face centered cubic structure was considered as the starting configuration for all $M_8K_6$ clusters where K atoms were placed at the centers of six faces and M atoms were placed at the eight corners of the unit cell. The self-consistent density for this configuration was calculated before starting the molecular dynamics simulations. To obtain the global minimum structure the cluster was heated up to 600 K and then cooled very slowly up to 0 K. To check whether the structure so obtained represents the global minimum structure, the system was reheated up to 800 K and allowing it to span for few thousands iterations followed by cooling it to 0 K to get the lowest energy structure. It was found that in both the cases, the lowest energy structure was the same, suggesting that it represented the true global minimum structure.

3. Results and Discussion

First we discuss the results of our calculations for two representative $K_{14}$ and $Al_{14}$ homoatomic clusters. The ground state structures obtained for both these clusters are shown in Fig. 1. The lowest energy structure comprises of a thirteen-atom icosahedron and the additional fourteenth atom caps one of the triangular faces of this icosahedron. For $K_{14}$ cluster, the minimum interatomic separation between potassium atoms is found to be 7.10 a.u. For $Al_{14}$ cluster, the minimum interatomic separation between Al atoms is found to be 4.85 a.u. A number of results are available in the literature and in all cases the ground state structure is an icosahedron with one of its face being capped by the additional Al atom. Our results are in good agreement with those reported by Kumar, using Car-Parrinello method where the values of interatomic separation and average binding energy per atom have been reported as 5.06 a.u. and 2.93 eV/atom, respectively. It needs to be mentioned that the objective of this paper is not to compare our results with ab-initio but to understand qualitatively the clustering behavior of different elements in heteroatomic systems.

For mixed metal clusters, containing eight atoms of Li or Na and six atoms of K, the structure is different from that of homoatomic fourteen atoms structure as can be seen from the comparison of Fig. 1 and Fig. 2. For mixed clusters, the eight Li or Na atoms form a highly distorted cubic structure and the six faces of it are capped from outside by K atoms. For $Li_8K_6$ cluster, the minimum interatomic separations between Li–Li and Li–K atoms are found to be 5.49 and 6.20 a.u., respectively. The corresponding separations for $Na_8K_6$ cluster are 5.52 and 6.70 a.u., respectively. For $Li_8K_6$ and $Na_8K_6$ clusters, the minimum K–K separation is found to be 8.35 and 11.10 a.u., respectively. Comparison of the K–K separations in these clusters with the corresponding sum of K atomic radius it seems that although there is a small interaction between K atoms in $Li_8K_6$ cluster however, there is practically no interactions between K atoms in $Na_8K_6$ cluster. The lowest energy structure of $Rb_8K_6$ and $Cs_8K_6$ clusters show different distribution of atoms from that of $Li_8K_6$ and $Na_8K_6$ clusters. The ground state geometries of $Li_8$, $Rb_8K_6$ and $Cs_8K_6$ are shown in Fig. 3. For $Rb_8K_6$ and $Cs_8K_6$ clusters, the six K atoms form an almost perfect inner octahedron and the eight faces of it are capped by Rb and Cs atoms in such a way that the cluster geometry is similar to that of a distorted FCC structure. The K atoms are placed at the face center positions of
the cube formed by eight Rb or Cs atoms. The outer cube formed by eight Cs or Rb atoms, is found to be slightly distorted as the Cs–Cs separation varies between 10.4 and 11.1 a.u. and the Rb–Rb separation is found to vary between 10.04 and 10.48 a.u. From the comparison of these interatomic separations with the sum of the corresponding atomic radii of the constituent elements, it is assumed that there is very weak interaction between Cs–Cs and Rb–Rb atoms for Cs8K6 and Rb8K6 clusters. For Cs8K6 cluster the interatomic separation between Cs and K atoms is approximately 7.74 a.u. and the average K–K separation is 7.23 a.u. For Rb8K6 cluster, the average interatomic separations between the Rb–K and K–K are 7.27 and 7.20 a.u., respectively. Thus for Rb8K6 and Cs8K6 clusters, six K atoms form an octahedron and eight Rb or Cs atoms are capping each triangular faces of this octahedron.

With a view to see the effect of capping of K6 cluster by Rb and Cs atoms similar calculations were carried out for homotomic K6 cluster and the results have been compared with those obtained for Rb8K6 and Cs8K6 clusters. The lowest energy structure for K6 cluster shows an octahedral geometry with K–K interatomic distance of 7.16 a.u. From the comparison of the interatomic separations for K6, Rb8K6 and Cs8K6, it is seen that the capping of K6 clusters by Rb or Cs atoms leads to slight distortion of the octahedral structure and finite expansion of the inner cluster cage formed by K6. To see the effect of the capping of Li8 cluster by six potassium atoms, similar calculations were carried out for the representative Li8 cluster and results are compared with those obtained for Li8K6 cluster. The ground state structure of Li8 cluster is shown in Fig. 2. This is a highly distorted cube type structure with minimum and maximum separation between the bonded Li atoms is 5.58 and 5.83 a.u. and each Li atom is bonded to four or five Li atoms. The average binding energy for the cluster is found to be 1.55 eV/atom. For Li8 a number of calculations based on different formalism, have been reported in the literature\(^{18-20}\) and results show significant variation. For example Sung \textit{et al.}\(^{18}\) have reported an unusual central trigonal prism with a capping atom as the lowest energy structure. Jones \textit{et al.}\(^{19}\) have reported that the ground state structure of Li8 has got D8h symmetry and is a pentagonal bipyramid with a lithium atom placed at the centre of the pentagon. Unlike both these reports, Rousseau \textit{et al.}\(^{20}\) have reported the Li8 structure as the capped tetrahedron with T2 symmetry and Li–Li interatomic separation being close to 4.80 a.u. This structure consists of two interpenetrating tetrahedron in such a way that the faces of the inner tetrahedron are capped by the other four Li atoms forming an outer tetrahedron. Thus it is clear that there exists a large variation in the ground state structures of Li8 cluster reported by different authors. The structure of Li8 cluster reported in the present study is quite different from those reported earlier. However, a comparison of the results obtained by using same formalism for Li8 and Li8K6 clusters, some inferences about the effect of capping of Li8 clusters by six K atoms can be drawn. It has been found that on capping of Li8 cluster by potassium atoms, the minimum and maximum interatomic separations between the bonded Li atoms are reduced to 5.49 and 5.75 a.u., respectively. Thus the capping of Li8 cluster by six potassium atoms leads to slight compression of the inner cage cluster, which is opposite to effect observed for inner K6 cage cluster in case of Rb8K6 and Cs8K6 clusters.

The opposite behavior of contraction and expansion of inner core clusters could be understood from the comparison of their atomic radius ratio. For example, in case of Li8K6 mixed cluster, the atomic radius ratio between K (outer surface) and Li (inner core) atoms is 1:1.5, whereas, for Cs8K6 cluster, the radius ratio between Cs (outer surface) and K (inner core) atoms is 1:1.1. The higher radius ratio between K and Li atoms helps outer K atoms to interact and thus forms more compact structure by reducing the separations between Li atoms. This fact is clear if we compare the interatomic distances (Table 1) between Li–Li or Na–Na in Li8K6 and Na8K6 cluster and Rb–Rb or Cs–Cs separations in Rb8K6 and Cs8K6 clusters. The distances between Li–Li atoms shows smaller than the sum of their atomic radius whereas the distances between Rb–Rb and Cs–Cs shows larger than their corresponding sum of the atomic radius. Thus the slight expansion or contraction of the inner core of the cluster on capping is related to the nature of the constituent elements and their corresponding atomic radius ratio. In order to understand the effect of the number of valence electrons of the constituent elements on the geometry of M8K6 clusters, similar calculations have been carried out for Al8, Mg8K6 and Al8K6 clusters. Figure 4 shows the ground state geometry of Al8, Mg8K6 and Al8K6 clusters. For both these bimetallic clusters, it is seen that the eight Mg or Al atoms form a highly distorted cubic structure and the six K atoms are capping its faces from outside. This is similar to what has been observed for Li8K6 and Na8K6 clusters and is consistent with the higher electronegativity values of Al and Mg in comparison to that of K atoms. The interatomic separation between the bonded Al–Al atoms is found to vary between 4.587 and 4.894 a.u., which is slightly different from that obtained for bare Al8 cluster. The minimum separation
between Al–K atoms is found to be close to 5.83 a.u. The average separation between K atoms is found to be 8.54 a.u. For Mg₉K₆ cluster, the eight Mg atoms form a highly distorted cubic structure and the interatomic separation between the bonded Mg atoms varies between 5.01 and 5.38 a.u. The minimum separation between Mg and K atoms is found to be 6.16 a.u. and between any two K atoms is close to 9.09 a.u., which indicates that there is no bonding between K atoms for Mg₉K₆ cluster. It is of interest to compare the structure of Al₈K₆ cluster with that of bare Al₈ cluster. Based on similar calculations it is observed that Al₈ forms a highly distorted cube type structure with Al–Al separation varying between 4.56 and 4.65 a.u. Each Al atom is connected to either four or five other Al atoms. It is of interest to mention that Jones, based on Car-Parinello method, has also reported a distorted cubic structure for Al₈ cluster. From the comparison of the results obtained for Al₈ and Al₈K₆ it is clear that the capping of Al₈ cluster by K atoms leads to slight expansion of Al–Al separations for the Al₈ core. This behaviour of interatomic separation between Al–Al atoms is opposite to that observed for Li–Li atoms in Li₅K₆ cluster. This implies that the number of valence electrons associated with the constituent elements play an important role in deciding the relative distribution of the constituent elements and their interatomic separations in bimetallic clusters. For Li₅K₆ cluster both Li and K are monovalent in nature and due to finite difference in their electronegativity values, some electron charge flows from K to Li and Li–Li separation is slightly reduced on capping by K atoms. Unlike this, for Al₈K₆ cluster, Al has got larger number of valence electrons in comparison to K and on bond formation between Al and K atoms in Al₈K₆ cluster, it is expected that finite charge may flow from Al towards K, thereby increasing the Al–Al interatomic separation. The relative distribution of Al, Mg and K atoms in these bimetallic clusters can also be understood in terms of electronegativity values of the constituent elements. Both Al and Mg are more electronegative than K and hence constitute the core of these bimetallic clusters. This is similar to what has been reported earlier for Li₅K₆ and Mg₉K₆ clusters.

Figure 5 shows the variation of the interatomic separation between the constituent atoms against the sum of their atomic radii for all these fourteen atom clusters to show the extent of bonding between these atoms. The points corresponding to Cs–Cs and Rb–Rb interatomic separations lie above the solid line which represents the variation of the sum of the atomic radii of the constituent atoms. This suggests that there is no bond formation between these atoms. Similarly, for Na₉K₆ and Mg₉K₆ the K–K separation is found to be significantly more than twice the atomic radius of K atom, indicating the absence of bonding between the K atoms. For Li₅K₆ and Al₈K₆ the observed K–K separation is 8.35 and 8.54 a.u., respectively which is just short of twice the atomic radius of K implying very weak bonding between the K atoms for both these clusters. Based on the results presented above, it is clear that for heteroatomic monovalent Mg₉K₆ clusters, the element, having smaller atomic radius and larger number of valence electrons form the inner cage of the cluster. Consequently, both Li and Na form the inner core of these fourteen atoms bimetallic Mg₉K₆ clusters. Unlike this, both Rb and Cs, which are less electronegative and have larger atomic radius than K, form the outer cage of the cluster. The result obtained for the Mg₉K₆ and Al₈K₆ clusters are also consistent with these inferences, as both Mg and Al, that are more electronegative and smaller in size than K, constitute the core of the clus-

---

Table 1 Values of the atomic radii, dimmer dissociation energies and cohesive energies of the constituent elements of M₉K₆ clusters and their interatomic separations.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₅K₆</td>
<td>2.98, 4.52</td>
<td>1.630, 0.934</td>
<td>1.04, 0.51</td>
<td>5.49 (5.96)</td>
<td>6.20 (7.50)</td>
</tr>
<tr>
<td>Na₉K₆</td>
<td>3.65, 4.52</td>
<td>1.110, 0.934</td>
<td>0.72, 0.51</td>
<td>5.52 (7.30)</td>
<td>6.70 (8.17)</td>
</tr>
<tr>
<td>K₉K₆</td>
<td>4.52, 4.52</td>
<td>0.934, 0.934</td>
<td>0.51, 0.51</td>
<td>7.10 (9.04)</td>
<td>10 (9.04)</td>
</tr>
<tr>
<td>Rb₉K₆</td>
<td>4.77, 4.52</td>
<td>0.852, 0.934</td>
<td>0.49, 0.51</td>
<td>10.05 (9.54)</td>
<td>7.27 (9.29)</td>
</tr>
<tr>
<td>Cs₉K₆</td>
<td>5.13, 4.52</td>
<td>0.804, 0.934</td>
<td>0.39, 0.51</td>
<td>10.42 (10.26)</td>
<td>7.74 (9.65)</td>
</tr>
<tr>
<td>Mg₉K₆</td>
<td>3.07, 4.52</td>
<td>1.510, 0.934</td>
<td>0.04, 0.51</td>
<td>5.07 (6.14)</td>
<td>6.15 (7.59)</td>
</tr>
<tr>
<td>Al₈K₆</td>
<td>2.75, 4.52</td>
<td>3.390, 0.934</td>
<td>1.51, 0.51</td>
<td>4.60 (5.50)</td>
<td>5.83 (7.27)</td>
</tr>
</tbody>
</table>

*These separations indicate that there is no bonding.

Numbers inside the bracket indicate the sum of atomic radii.
results and those reported earlier\(^8\) for a variety of \(A_2B_2\) bimetallic clusters, the distribution of the two types of elements in bimetallic clusters, has been rationalised in terms of the values of the electronegativity, atomic size and cohesive energy of the constituent elements. The element with higher values of electronegativity, cohesive energy and smaller atomic size, forms the core of such bimetallic clusters. This leads to the reduction of charge density over the surface of such bimetallic clusters.

**REFERENCES**


**4. Conclusions**

In conclusion we would like to mention that in this study, the ground state geometry for a number of bimetallic \(M_2K_6\) clusters has been reported. The structure of the homo and hetero atomic clusters, containing fourteen atoms, are found to be completely different. Based on the analysis of present