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Compound clusters of heavy post-transition elements

Stable analogues to Zintl polyanions and molecules

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Neutral binary clusters of Pb–As, Pb–Se, Pb–Te, Bi–In and Bi–Te are generated by inert gas condensation in a double oven source and probed by electron impact. Cluster ions corresponding to the Zintl polyanions Pb_5^{2-} and Pb_9^{4-} with respect to atom and valence electron number, are strongly enriched by electron induced dissociation ($(Pb_2As_3)^+$, $(Bi_4In)^+$, $(Pb_4As_5)^+$, $(Bi_7In_2)^+$). For the corresponding systems, no other compound cluster ions are enriched in a comparable manner. Enhanced stability is found for $(Pb_{n-1}As)^+$ ($n=7$, 10, 13) and $(Bi_3Te)^+$, which are isoelectronic with neutral 'magic' Pb_n clusters and the very stable Bi_4 molecule, respectively.

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Introduction

How does chemical bonding work in finite systems containing only a few atoms? Cluster stability, as a result of more or less favorable electronic and geometric configurations, allows to probe chemical bonding by mass spectrometric means. The stability of neutral clusters and cluster ions leads to abundance maxima either as a result of the nucleation process or of the dissociation during the ionization process. The former can be estimated from low energy electron ionization or one photon ionization which, under favourable conditions, reflect the *neutral* cluster abundances. High energy electron ionization, on the other hand, causes electron induced dissociation (EID) and populates stable *ions*. The stability of certain configurations of atom and valence electron number for cluster polyanions of heavy post-transition elements was confirmed by Zintl's early work [1 b]. Later work produced single crystals of organic salts containing these polyanions, called Zintl ions from that time on, and allowed to determine their structure by X-ray scattering [1 a]. More Zintl ions were found and research extended to Zintl cluster *analogues*, an abbreviation we use henceforth to denote configurations possessing identical *numbers* of valence electrons and identical *numbers* of atoms. Free cluster analogues have been investigated since 1985. Especially stable binary clusters which are analogous to the Zintl polyanions Pb_5^{2-} and Pb_9^{4-} are observed for the Pb–Sb [2–4], Sn–Bi [2, 4], and Sn–As [4] systems. The stability of Pb and Sn cluster polyanions was confirmed using Cs or Rb adatoms as electron donors [5]. The conclusion may be that the stability of free heavy post-transition metal clusters is maintained by analogy. In order to decide if analogy can predict stability in a general sense, it is necessary to adjust the configurations of atom and valence electron numbers, which can be realized by binary clusters. We examined Pb–As which is isoelectronic with Pb–Sb, but also the Pb–Se, Pb–Te, Bi–In and Bi–Te cluster systems.

Experimental

Binary compound clusters are generated by evaporating the elements from two separated resistively heated crucibles and by quenching the vapors in cold helium gas (80 K, 50–100 Pa) (Fig. 1). A beam of neutral clusters leaves the condensation cell via a differentially pumped section. The clusters are ionized by a pulsed electron beam within a field free region. After the end of the electron pulse the ions are accelerated into

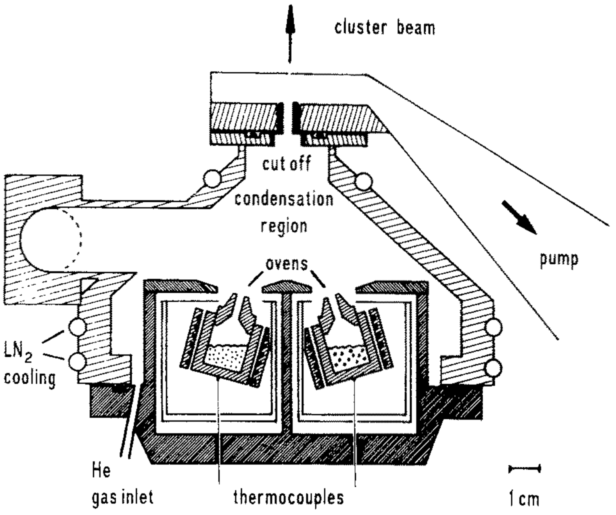

Fig. 1. Cluster source for the generation of binary clusters. The vapor pressure of each component is adjusted via the temperature of the two independently heated crucibles. The helium pressure in the condensation cell is measured by a difference manometer and regulated by a needle valve for typ. 0.5 to 1 Torr

the ion optics of the time-of-flight mass spectrometer [6]. The electron energy E_i is varied between 8 and 100 eV. Electron energies chosen close to the appearence potentials of the clusters provide a low fragmentation probability [3, 7] and allow the neutral cluster size distribution to be estimated by means of the mass spectra obtained. High energy electron ionization enhances the abundance of comparatively stable cluster *ions* by EID taking place before mass analysis, i.e. within the first one or two microseconds after ionization.

Results and discussion: Pb – As clusters

Electronically, the Pb – As system corresponds to the Pb – Sb system investigated in a former work [3], since As and Sb are isoelectronic. The spectrum recorded at low electron energy preferentially shows compound clusters $Pb_nAs_4^+$ and $Pb_nAs_2^+$. Since arsenic evaporates mainly as tetramers at the oven temperatures applied the $Pb_nAs_2^+$ clusters are formed by dissociative chemisorption. Similar to the Pb – Sb system [3] the products contain an even number of valence electrons *before* ionization.

Neutral analogues to the Zintl polyanions Pb_5^{2-} and Pb_9^{4-} are the Pb_3X_2 and Pb_5X_4 (X = As, Sb) compound clusters. Within the Pb – Sb mass spectra, the Pb_3Sb_2 cluster marks a step in the dissociation probability and Pb_5Sb_4 is observed with the highest ion abundance [3]. However, Pb – As mass spectra recorded at low electron energy do not show these cluster analogues with enhanced intensities (Fig. 2a). It has to be noted that enhanced stability is more difficult to display for neutral clusters than for ions. If the condensation conditions do not provide a stability test, i.e. if the dissociation probability during condensation is low, high stability is not necessarily reflected by an enhanced abundance in the neutral beam.

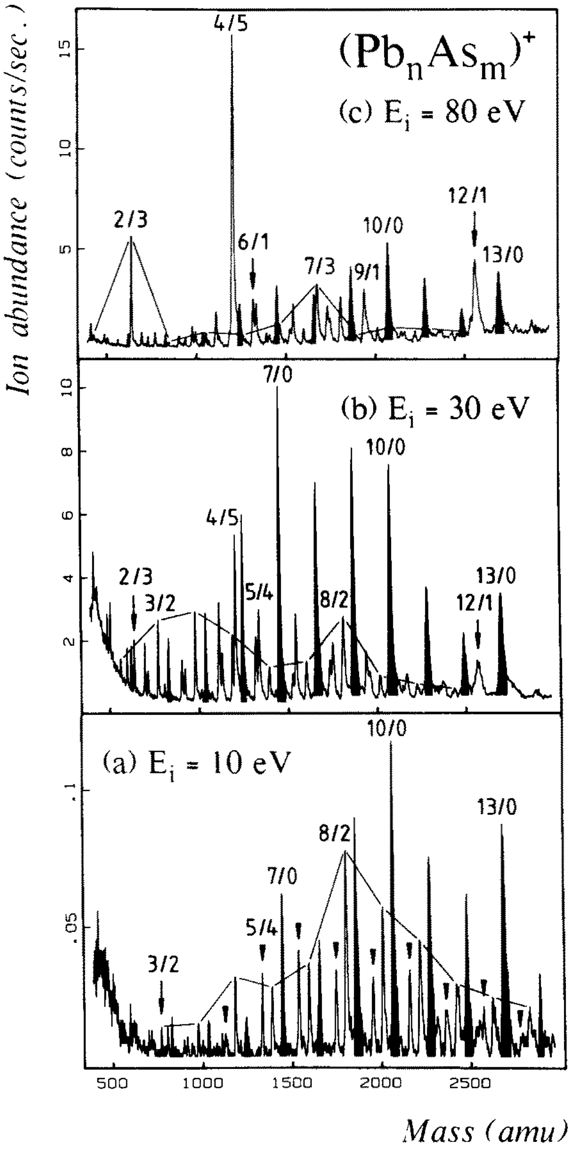

Fig. 2a–c. Mass spectra of $(Pb_nAs_m)^+$ clusters recorded at different electron energies E_i. Filled peaks correspond to pure Pb_n^+ clusters, Pb_nAs_4 clusters are marked by triangles (**a**). Dissociative chemisorption of As_4 molecules on Pb_n clusters results in Pb_nAs_2 compound clusters (connected by solid lines in **a** and **b**). At high electron energies (**b, c**), EID enriches the Zintl clusters $(Pb_2As_3)^+$ and $(Pb_4As_5)^+$. Peaks connected by solid lines (**c**) refer to the $(Pb_nAs_3)^+$ ion sequence with maxima for $n=3$ and 7. The $(Pb_7As_3)^+$ ion (**c**) is isoelectronic with the Pb_8As_2 cluster observed at low electron energy (**a**)

At higher electron energies (Fig. 2b) the lines of $(Pb_2As_3)^+$ and $(Pb_4As_5)^+$ emerge and dominate the

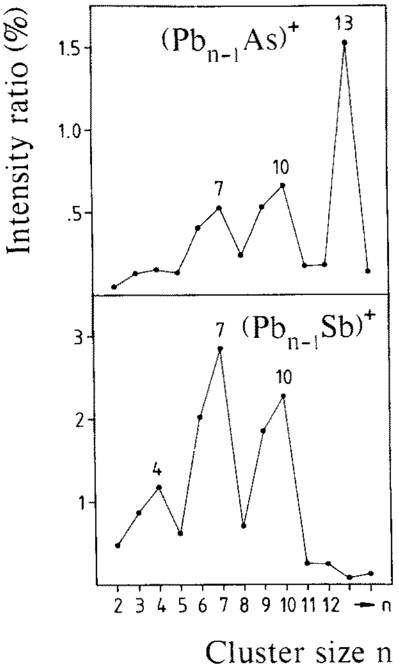

Fig. 3. Integrated ion abundances of the $(Pb_{n-1}X)^+$ (X = Sb, As) sequences in per cent of the whole ion signal obtained at $E_i = 80$ eV. The $(Pb_{n-1}X)^+$ ions are isoelectronic with neutral Pb_n clusters. Within both sequences maxima occur for $n = 7$ and 10. A maximum at $n = 13$ is observed within the $(Pb_{n-1}As)^+$ sequence exclusively

mass spectrum (Fig. 2c), similar to the findings for the isoelectronic Pb–Sb system [3]. The strong intensity enhancement requires larger cluster sizes to contribute to these two ions by EID. Moreover, EID enhances the sequences $(Pb_nAs)^+$ and $(Pb_nAs_3)^+$, which contain an even number of electrons *after* ionization.

Since the arsenic atom contributes one more valence electron than the lead atom, Pb_n and $(Pb_{n-1}As)^+$ are isoelectronic. This explains why the magic numbers of neutral lead clusters $n = 7$, 10 and 13 [8] are reproduced by maxima of $(Pb_{n-1}As)^+$ after EID (Fig. 3). However, a difference between the Pb–As and the Pb–Sb system occurs for $n = 13$: while the abundance of the $(Pb_{12}As)^+$ ion is strongly enhanced it remains low for $(Pb_{12}Sb)^+$ (Fig. 3). This difference underlines the importance of *electronic* as well as *structural* properties in cluster physics, as will be explained in what follows.

The enhanced stability of Pb_{13} can be explained by a close-packed *hcp* or *fcc* shell closing (atoms considered as hard spheres) but, from energetic reasons [9] the structure is more likely to be an icosahedron. However, the center atom within an icosaeder undergoes compression. Its radius has to be about 9.5% smaller than for an atom located in the outer shell [10], i.e. $R = 1.33$ Å instead of $R_{cov.}(Pb) = 1.47$ Å [11]. Here the advantage of *As as a central* atom becomes evident since its radius ($R_{cov.}(As) = 1.20$ Å [11]) is small enough to provide a replacement of Pb without compression, which is not the case for Sb($R_{cov.}(Sb) = 1.40$ Å). Therefore we explain the predominant production of $(Pb_{12}As)^+$ at EID by the production of stable isosaeders with As as a central atom. Excess atoms are losely bound on this closed configuration and desorb easily. The clusters $n = 7$ and 10 are not sensitive to the atomic radii, which agrees with the fact that they consist of surface atoms exclusively, in contrast to $n = 13$ which is the smallest cluster with a closed shell around a center atom.

Since the $(Pb_{12}Sb)^+$ ion is not enriched by EID although the antimony atom is smaller than the lead atom, one may conclude that the contribution of EID to the abundance of Pb_{13}^+ in pure lead cluster mass spectra is also small and that the maximum at Pb_{13}^+ [8] is due to an already enhanced abundance of Pb_{13} in the neutral beam.

The $(Pb_7As_3)^+$ ion shows up as a local maximum within the sequence $(Pb_nAs_3)^+$ (Fig. 2c). It is isoelectronic with the neutral Pb_8X_2 cluster which is observed as a maximum at low E_i (X = As (Fig. 2a), X = Sb [3]). The Pb_8X_2 and $(Pb_7X_3)^+$ clusters are isoelectronic with the $TlSn_9^{3-}$ polyanion, for which a bicapped square antiprismatic structure was determined [1a].

Pb – Se and Pb – Te clusters

Within the Pb–Se and Pb–Te cluster systems, the isoelectronic analogues to the Zintl polyanions Pb_5^{2-} and Pb_9^{4-} are the neutral Pb_4X and Pb_7X_2 (X = Se, Te) clusters. Since the elements X contribute two p-electrons more than Pb, no singly charged analogues can be obtained by substitution. The Pb_7X_2 clusters are observed with high ion abundances in mass spectra recorded at low electron energies (Figs. 4a, 5a). The Pb_nX sequences show the Pb_9X clusters as relative maxima which are isoelectronic with Pb_8As_2, $(Pb_7AS_3)^+$ and with the polyanion $TlSn_9^{3-}$.

At high energy electron ionization, EID moderately enhances the abundances of $(Pb_4X_4)^+$ ions and various selenium rich Pb–Se cluster ions containing primarily 4, 5, 6 and 7 selenium atoms for which no Zintl ions are known. Within the $(Pb_nSe_4)^+$ sequence the $(Pb_4Se_4)^+$ ion (Fig. 4b) marks a local maximum and the onset of selenium rich $(Pb_4Se_n)^+$ clusters. For Pb–Te, the $(Pb_4Te_4)^+$ ion (Fig. 5b) is the maximum within the clusters containing eight atoms as well as within the $(Pb_nTe_4)^+$ and $(Pb_4Te_n)^+$ sequences. Former work on Pb–X (X = S, Se) clusters generated by a free jet expansion [12] showed $(Pb_4X_4)^+$ as the

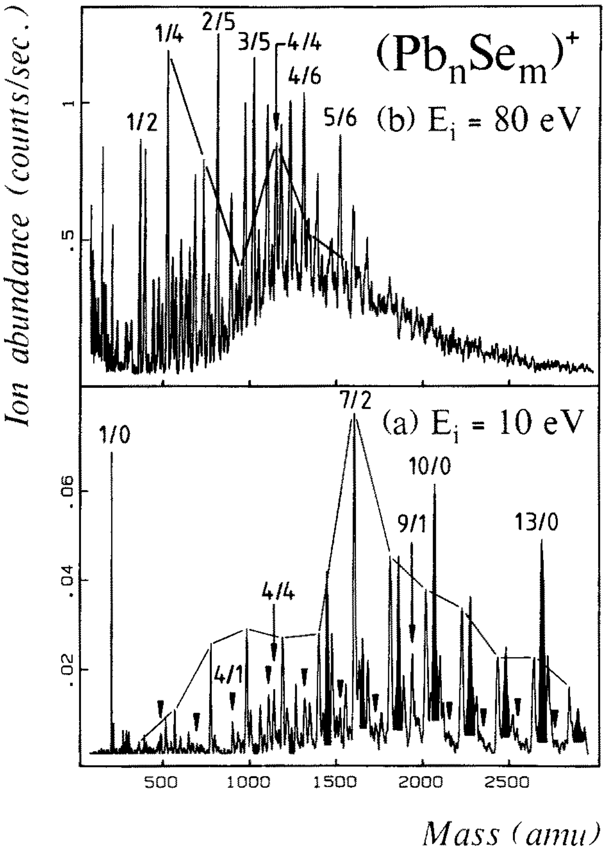

Fig. 4a and b. Mass spectra of $(Pb_nSe_m)^+$ clusters at 10 eV (**a**) and 80 eV (**b**). Peaks referring to the $(Pb_nSe_2)^+$ sequence in (**a**) and to the $(Pb_nSe_4)^+$ sequence in (**b**) are connected by solid lines. Lines corresponding to pure lead and Pb_nSe clusters are colored black and marked by triangles, respectively

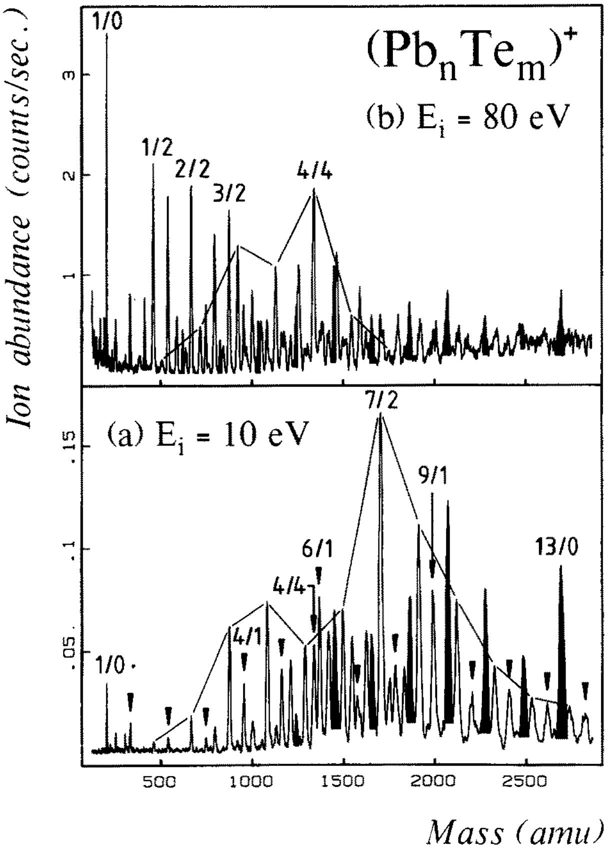

Fig. 5a and b. Mass spectra of $(Pb_nTe_m)^+$ clusters recorded at 10 eV (**a**) and 80 eV (**b**). The lines of pure lead clusters are colored black, the $(Pb_nTe_2)^+$ (a) and the $(Pb_nTe_4)^+$ (**b**) sequences are connected by solid lines. The Pb_nTe sequence produced by dissociative chemisorption of Te_2 on lead clusters is marked by black triangles

most abundant ion containing more than five atoms. In analogy to the corresponding bulk lattices the authors suggested a cubic structure. Moreover, covalent bonds along the edges of the cube may contribute to the stability of this cluster. Equilibrium vapor of Pb–Te, Pb–Se [13] and Pb–S [14] does not contain Pb_4X_4 (X = Te, Se, S) but Pb_4O_4 was found within the vapor of PbO [15]. These findings can be due to the enhanced stability of *neutral* Pb_4X_4, which is reflected by a corresponding enhanced ion signal [12]. The enrichment of $(Pb_4X_4)^+$ by EID (Figs. 4b, 5b), however, demonstrates the extraordinary stability of the *ion* as well, although it contains an odd number of electrons. The ion's stability agrees with the observation that $(Ge_4Te_4)^+$ possesses a stronger relative intensity than Ge_4Te_4 after laser vaporization of solid GeTe [16].

Bi–In clusters

Analogues to the Zintl polyanions Pb_5^{2-} and Pb_9^{4-} within the Bi–In system are the ions $(Bi_4In)^+$ and $(Bi_7In_2)^+$. These two cluster configurations are also present in mass spectra recorded at low electron energy (Fig. 6a) as they can be generated during condensation by adsorption of indium atoms on Bi_n clusters. As a result of EID (Fig. 6b) they are the most abundant compound cluster ions within the mass spectrum. The enrichment of these two Zintl analogues by EID is comparable with the Pb–As and Pb–Sb systems. However, the maximum intensity is already obtained at lower electron energies (Fig. 7) than for the Pb–Sb system [3], which indicates a lowered threshold energy for EID.

This example illustrates that stability is not only maintained for *atoms* replaced by isoelectronic ones, but also for isoelectronic *combinations* of atoms. i.e. that for the clusters of post-transition elements the criterion for stability is the number, but not the origin of the electrons forming the cluster's bond system. Especially, the stability of Zintl clusters is not limited to species containing group IVa elements. The isoelectronic Bi_5^{3+} and Bi_9^{5+} polycations were found to possess enhanced stability, but slightly different geometrical structure [1a]. Thus $(Bi_4In)^+$ and $(Bi_7In_2)^+$ can be obtained as the result of a substitution of one and

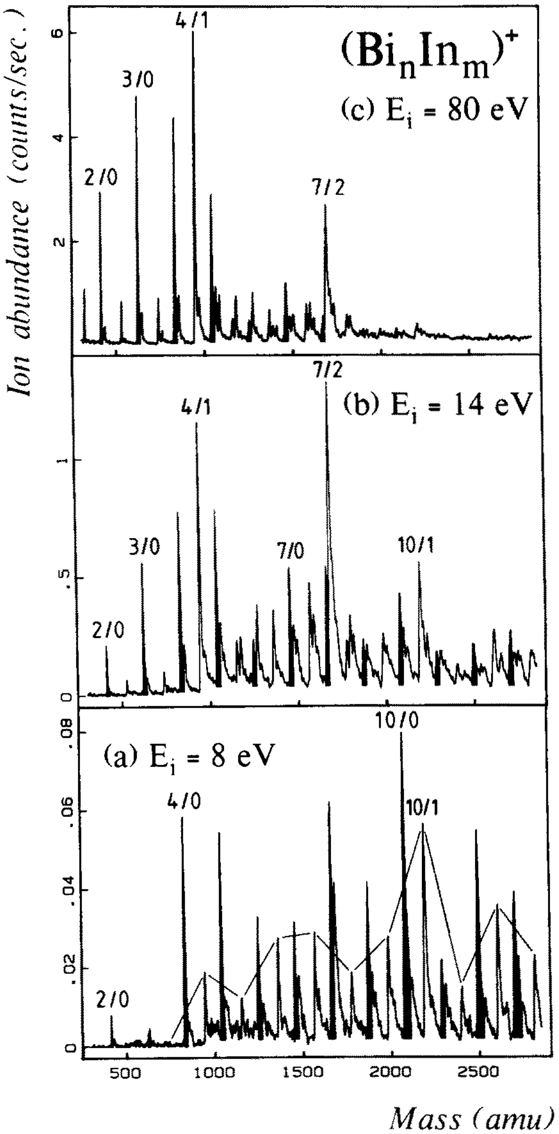

Fig. 6a–c. Mass spectra of $(\mathrm{Bi}_n\mathrm{In}_m)^+$ clusters recorded at different electron energies E_i. Filled peaks correspond to pure bismuth clusters. The lines of the predominant $\mathrm{Bi}_n\mathrm{In}$ compound clusters are connected by solid lines (**a**). Within the mass spectra at 14 eV and 80 eV (**b, c**) the two strongest lines of the compound clusters correspond to the Zintl analogues $(\mathrm{Bi}_4\mathrm{In})^+$ and $(\mathrm{Bi}_7\mathrm{In}_2)^+$

two bismuth atoms from the polycations by indium atoms, respectively.

In addition, the Bi_4 cluster is observed with enhanced ion abundance whereas Bi Knudsen vapor shows only a small fraction of Bi_4 molecules [7]. Its enhanced stability as a neutral cluster will be discussed below.

Bi – Te clusters

Like other combinations of group Va/VIa atoms, the Bi – Te system does not allow for the construction of neutral or singly ionized compound cluster analogues corresponding to Pb_5^{2-} and Pb_9^{4-}. However, they allow to produce configurations which cannot be constructed using IIIa/Va or IVa/Va elements. One of these configurations is the $(\mathrm{Bi}_3\mathrm{Te})^+$ cluster ion, which is isoelectronic to the neutral tetramers of As,

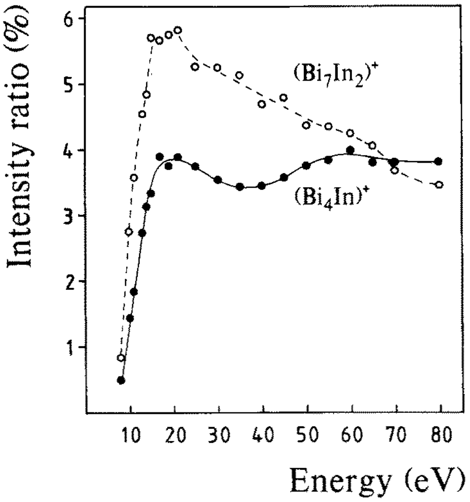

Fig. 7. Electron energy dependence of the intensity of the $(\mathrm{Bi}_4\mathrm{In})^+$ and $(\mathrm{Bi}_7\mathrm{In}_2)^+$ Zintl analogues in per cent of the total ion signal. Oven temperatures applied are 896 K (Bi) and 1194 K (In)

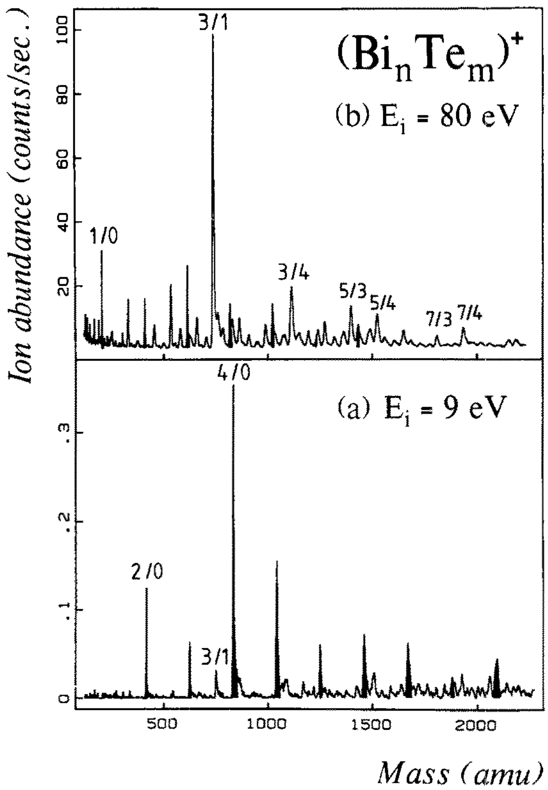

Fig. 8a and b. Mass spectra of $(\mathrm{Bi}_n\mathrm{Te}_m)^+$ clusters recorded at 9 eV (**a**) and 80 eV (**b**). The peaks of pure bismuth clusters are colored black. Ionization at high electron energies enriches the $(\mathrm{Bi}_3\mathrm{Te})^+$ ion (**b**) which is isoelectronic with the neutral Bi_4 cluster represented by a maximum at low E_i (**a**)

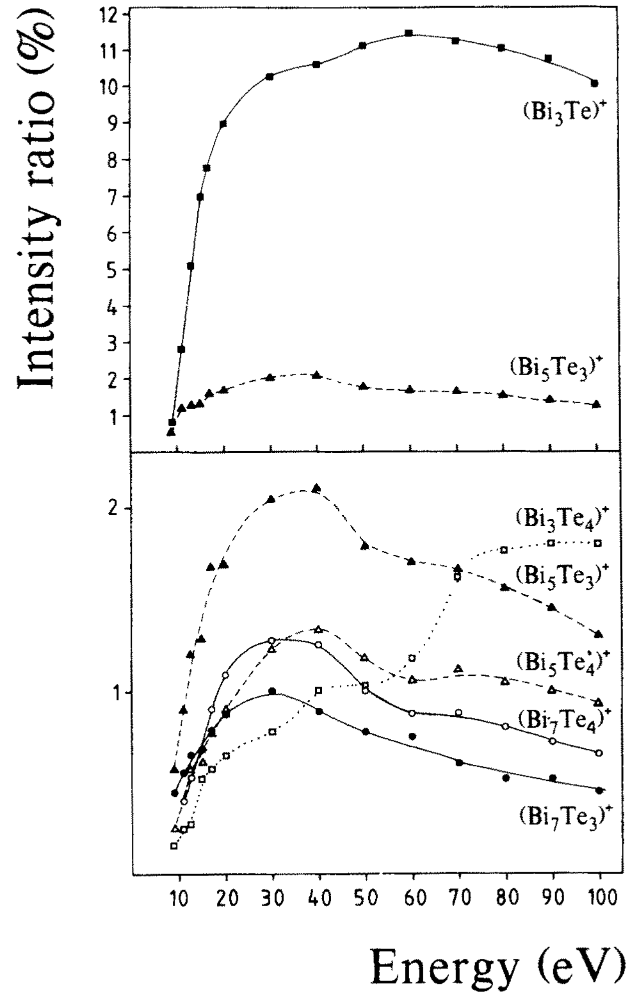

Fig. 9. Electron energy dependence of the relative intensity of $(Bi_3Te)^+$ and less abundant ions enhanced by EID in per cent of the total ion signal. Oven temperatures applied are 976 K (Bi) and 516 K (Te)

Sb and Bi and with the $Pb_2Sb_2^{2-}$ polyanion [17]. These neutral species display their enhanced stability either by being the main component of the equilibrium vapor (As, Sb [3]) or by an enhanced abundance as a result of nucleation (Bi, Figs. 6a, 8a).

EID proves the extraordinary stability of the $(Bi_3Te)^+$ *ion* by strong intensity enhancement (Figs. 8b, 9). Laser vaporization of Va/VIa compounds, for instance, showed strong ion signals for $(As_3X)^+$, $(Bi_3X)^+$, $(Sb_3X)^+$ (X = S, Se, Te), $(Sb_2BiTe)^+$ and $(SbBi_2Te)^+$ ions [16], which are isoelectronic to $(Bi_3Te)^+$. From our results we conclude that their intensity enhancement represents the enhanced stability of these charged species and is due to dissociation of cluster *ions*.

Another stable ion is $(Bi_3Te_4)^+$ (Figs. 8b, 9). It is isoelectronic with the Sb_7^{3-} polyanion [1], with the P_4S_3 molecule [19] and with the $(As_3X_4)^+$ (X = O, S, Se), $(Sb_3O_4)^+$, $(Sb_3S_4)^+$, $(Bi_3O_4)^+$, $(As_3S_3Se)^+$, $(As_3S_2Se_2)^+$ and $(As_3SSe_3)^+$ ions known from laser evaporated Va/VIa compounds [16, 18]. Its relative intensity steadily increases with increasing electron energy, in contrast to other ions populated by EID (Fig. 9), most of which are not Zintl analogues ($(Bi_5Te_3)^+$, $(Bi_7Te_3)^+$, $(Bi_7Te_4)^+$, but $(Bi_7Te_4)^+$ is isoelectronic with As_{11}^{3-} and P_{11}^{3-} [1]).

Twofold ionized analogues

Analogy, applied to twofold ionized compound clusters, predicts an enhanced stability for $(PbX_4)^{++}$, $(Pb_3Z_2)^{++}$, $(Pb_3X_6)^{++}$, and $(Pb_6Z_3)^{++}$ (X = As, Sb; Z = Se, Te). However, no corresponding lines are found within the mass spectra. This result can be explained by former results on twofold charged lead clusters investigated unter the same conditions. In addition to a stability threshold of $n \approx 30$ lead atoms, twofold charged cluster ions have been found for $n = 7$ to 13 [8c, 20], the stability of which has been explained by a linear geometrical structure allowing for the maximum distance between the two charges [20]. Since Zintl analogues do not occur as linear configurations [1a], twofold ionized analogues below the stability threshold ($n \approx 30$) easily dissociate by Coulomb explosion and cannot be enriched by EID.

Conclusion

The observation of stable Zintl clusters for various atomic combinations shows that the stability of heavy post-transition compound clusters depends primarily on the number of atoms and valence electrons contained in the *clusters*. EID results show that the exceptional stability of Zintl analogues is maintained regardless of distortions due to different atomic radii and valence electron numbers of the different *components*. However, of the large number of Zintl polyanions known from complex chemistry only few ligand-free polyions are reproduced by stable free cluster analogues (Table 1). Especially, the cluster analogues of Pb_5^{2-} and Pb_9^{4-} are abundant products of the nucleation and the fragmentation processes. The results of EID on $(Pb_{12}X)^+$ demonstrate the sensitivity of cluster stability on atomic radii for clusters containing non-surface atoms and underline that Pb_{13} cluster analogues possess an icosahedral structure. EID enhanced ion abundances of $(Pb_{n-1}As)^+$ (n = 7, 10, 13) clusters reflect the stability of their neutral cluster analogues Pb_7, Pb_{10} and Pb_{13}.

Table 1. Cluster analogues to Zintl polyions constructable as neutrals or ions. References for experimental observation are included in the last column. [−] indicates clusters which have not yet been observed with enhanced stability

Zintl polyions known from complex chemistry	Compound clusters		Reference *: this work
	Neutrals	Ions	
$Pb_2Sb_2^{2-}$, Pb_4^{4-}, Sn_4^{4-}, TI_4^{8-},$TI_2Te_2^{2-}$, P_4, As_4, Sb_4, Bi_4 4 atoms, 12 *p*-electrons	Bi_4, Sb_4, As_4	$(Bi_3Te)^+$ etc.	[16, 18, *]
Pb_5^{2-}, Sn_5^{2-}, $PbSn_4^{2-}$, Bi_5^{3+} 5 atoms, 12 p-electrons	Sn_3As_2	$(Sn_2As_3)^+$ [−]	[4]
	Sn_3Bi_2	$(Sn_2Bi_3)^+$	[4]
	Pb_3Sb_2	$(Pb_2Sb_3)^+$	[2–4]
	Pb_3As_2 [−]	$(Pb_2As_3)^+$	[*]
	Pb_4Se, Pb_4Te [−]	–	[*]
	–	$(Bi_4In)^+$	[*]
As_7^{3-}, Sb_7^{3-}, Bi_7^{3-} 7 atoms, 24 *p*-electrons	–	$(Bi_3Te_4)^+$	[*]
Pb_9^{4-}, Sn_9^{4-}, Ge_9^{4-}, Bi_9^{5+}, $Pb_xSn_{9-x}^{4-}$, $Sn_xGe_{9-x}^{4-}$, $TISn_8^{4-}$, Sn_8Sb^{3-} 9 atoms, 22 *p*-electrons	Sn_5As_4	$(Sn_4As_5)^+$	[4]
	Sn_5Bi_4	$(Sn_4Bi_5)^+$	[2, 4]
	Pb_5Sb_4	$(Pb_4Sb_5)^+$	[2–4]
	Pb_5As_4 [−]	$(Pb_4As_5)^+$	[*]
	Pb_7Se_2, Pb_7Te_2	–	[*]
	–	$(Bi_7In_2)^+$	[*]
$TISn_9^{3-}$ 10 atoms, 22 *p*-electrons	Pb_8Sb_2	$(Pb_7Sb_3)^+$ [−]	[3]
	Pb_8As_2	$(Pb_7As_3)^+$	[*]
	Pb_9Te, Pb_9Se	–	[*]

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