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Formation, growth mechanism and packing sequences of binary alloy cluster anions from laser ablation of mixtures of lead and transition metals

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By using laser ablation of the mixtures of a transition metal (M: Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pd, Ag) plus lead, M/Pb binary cluster anions were observed except for Zn, and the number of transition metal atoms contained in the binary clusters is at most 4. This behavior is different from that reported previously for M/Ge binary clusters. The experiments indicate that it is also very difficult to form Al/Pb clusters. The distribution patterns of M/Pb binary alloy cluster anions are remarkably similar to those of pure Pb clusters, consistent with a formation mechanism in which transition metal atoms are sequentially attached to $[M_{x-1}Pb_y]^-$ clusters and thus form $[M_xPb_y]^-$ clusters by a simple condensation process. As the number of transition metal atoms increases, the intensities of binary clusters gradually decrease. It is proposed that $[MPb_4]^-$ and $[MPb_5]^-$ cluster anions might be the unit building blocks of M/Pb binary cluster anions, and the layer packing sequences for magic clusters are predicted on this basis. The $[M_xPb_y]^-$ binary clusters containing 13 atoms ($x + y = 13$; $x \neq 0$) are proposed to have an icosahedral structure. Copyright © 2003 John Wiley & Sons, Ltd.

Clusters of group 14 elements have drawn great interest and have been studied both experimentally and theoretically by a number of researchers. In particular, lead clusters have been produced by a variety of techniques. Lead is one of the most abundant heavy metals in the environment. Due to its nature as a relatively volatile and significant impurity in ores, as well as to its use as a gasoline additive, lead and lead particles are released into the environment. An important application of lead and lead oxide is in the manufacture of lead-acid batteries.

In a more recent context, the interest in surfactant-mediated two-dimensional (2D) layer-by-layer growth, for both semiconductor and metal systems in heteroepitaxy and homoepitaxy, is increasing.[1–6] It is known that preadsorption of suitable surfactants such as As, Sb and Te can change the mode of Ge growth on Si (100) from three-dimensional (3D) cluster growth to 2D layer-by-layer growth.[1,2] A surfactant used to induce layer-by-layer growth mode in epitaxy should firstly always float on the surface during epitaxy growth. This property means that the surfactant should have smaller free energy. Secondly, a suitable surfactant must also perform one of the two crucial functions, namely, effectively reduce adatom interlayer diffusion, or enhance adatom interlayer diffusion. Because the surface free energy of an inactive Pb layer is smaller, Pb can be used as a surfactant during the growth process of thin films to promote 2D layer-by-layer growth. Camarero *et al.*[7,8] demonstrated that a monolayer of Pb can suppress twinning in Cu(111) by molecular beam epitaxy, an effect with important implications for oscillatory magnetic coupling[9] and the related giant magnetoresistance.[10] However, due to interdiffusion and formation of alloys[11] during the growth of thin films for miscible metal atoms at metal/metal interfaces, it is believed that this kind of surface alloying phenomenon on solid surfaces may have an unfavorable effect on the activation process, and will strongly affect the properties of thin films. The most interesting aspect is that the immiscible metals can also develop surface alloy formation.

Because of their importance both in fundamental theory and practical technology, it is important to study the clustering behavior and stable compositions in the gas phase of binary alloy clusters containing elemental lead and other metals. Studies of these alloy clusters would make some contribution to investigations of the mechanisms of epitaxy, and might also help to effectively reduce the alloying phenomenon in 2D layer-by-layer growth. In addition, these studies in the finite-size regime of the clusters would shed additional light on the microscopic basis for the properties of Pb/M alloys. In this paper, a series of binary alloy cluster anions, produced by laser ablation of mixtures of M/Pb (where M denotes a metal), were studied using a tandem time-of-flight (TOF) mass spectrometer. The stable compositions and the size distributions in binary alloy cluster ions are discussed, and the structures of magic clusters are proposed.

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EXPERIMENTAL

The binary alloy cluster ions composed of elemental lead and another metal were generated and analyzed under the following conditions. The samples were prepared with lead (purity 99.8%) and transition metal (purity > 99%) powders, mixed well in different molar ratios and pressed into tablets. The experiments to produce and detect M/Pb binary cluster ions were performed using the first stage of a home-made tandem time-of-flight mass spectrometer (T-TOF MS) with a vaporization laser. A detailed description of the T-TOF MS has been given elsewhere.[12] Briefly, the second harmonic of a Q-switched Nd:YAG laser (532 nm, 10 mJ/pulse, 10 pulses/s) was focused on the surface of a tablet sample held in the vacuum chamber (at 10^{-6} Torr) of the spectrometer to produce the cluster ions. The cluster ions were extracted and accelerated with a pulse voltage of 0.1 and 1.1 kV, respectively, and then drifted in a field-free region 3.5 m long. The cluster ions were detected by a dual microchannel plate detector at the end of the field-free region, and recorded by a PC computer to give the mass spectrum. The mass resolution of the first stage of the T-TOF MS is about 300. Typically, 1000–2000 laser shots were accumulated and stored in the computer.

RESULTS AND DISCUSSION

In our previous publications, the compositions and distributions of Co/Pb binary alloy clusters were reported in detail.[13] Here we report the study of M/Pb magic clusters, and the mechanism of cluster growth and packing sequences. In order to make a direct comparison between pure $[Pb_y]^-$ clusters and $[Co_xPb_y]^-$ binary alloy clusters, and to take into account the effect of the concentration of lead in the samples, the intensities of pure $[Pb_y]^-$ clusters are always defined as 100. The relative intensities of Co/Pb binary alloy clusters are plotted as a function of cluster size y for different values of x and sample molar ratio (see Figs. 1 and 2).

Figure 1 shows the relative intensities of $[Co_xPb_y]^-$ binary alloy clusters resulting from the sample with molar ratio Pb/Co = 1:1. As seen in Fig. 1, for cluster series $[Co_xPb_y]^-$ with the same number (y) of Pb atoms, the relative intensities

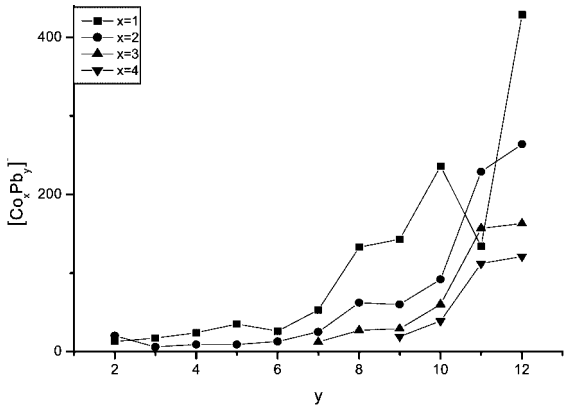

Figure 1. Relative intensities of $[Co_xPb_y]^-$ binary alloy clusters resulting from laser ablation of a sample with molar ratio Pb/Co = 1:1. The absolute intensities of $[Pb_y]^-$ (i.e. x = 0) are defined as 100 in each case.

always decrease with the number of cobalt atoms (x) except for y = 11. When the number of lead atoms (y) is larger than 7, the intensity of cluster series $[CoPb_y]^-$ is higher than that of pure $[Pb_y]^-$ clusters. However, for $[Co_xPb_y]^-$ (x = 2–4) cluster series, the intensities are not higher than those of pure $[Pb_y]^-$ until y is larger than 10.

Generally speaking, under these conditions metal clusters grow or dissociate by a simple condensation or evaporation process where growth or fragmentation proceeds almost exclusively by adding or losing single metal atoms.[14] Due to the metallic nature of lead and cobalt, it is postulated that Co/Pb binary clusters grow in the same way. With increasing numbers (x) of Co, the intensities of $[Co_xPb_y]^-$ clusters with the same value of y (except y = 11) gradually decrease. Thus, the growth mechanism of Co/Pb binary clusters is proposed to be as follows:

$$Co + \left[Co_{x-1}Pb_y\right]^- \rightarrow \left[Co_xPb_y\right]^- \quad \text{for } x \geq 1.$$

That is to say, Co atoms sequentially attach to $[Co_{x-1}Pb_y]^-$ clusters and thus form $[Co_xPb_y]^-$ clusters. Therefore, the formation rate of $[Co_xPb_y]^-$ clusters depends on the concentration of the $[Co_{x-1}Pb_y]^-$ cluster. In this process, the formation of pure lead cluster anions is proposed to be the rate-determining step so that the distribution with respect to y can be the same for the pure Pb clusters as for the mixed Pb/Co clusters. In addition, we observed that the relative intensity of the $[Co_2Pb_{11}]^-$ cluster is higher than that of $[Co_xPb_{11}]^-$ (x = 1, 3, 4), emphasizing the special stability of this cluster ion.

The relative intensities of $[CoPb_y]^-$ and $[Co_2Pb_y]^-$ binary alloy cluster series, for different sample molar ratios, are given in Figs. 2(A) and 2(B). The shapes of the curves for the $[CoPb_y]^-$ and $[Co_2Pb_y]^-$ cluster series remain unchanged on changing the molar ratio. When the number of lead atoms $y \leq 7$, these two kinds of cluster series show little change in yield (intensity) with the sample composition. However, when the number of lead atoms y > 7, there is a larger change on varying sample composition. If the lead content in the sample is too large or too small, lower relative intensities are always observed. This indicates that the concentration of Co or Pb in the plasma has little effect on the distribution and relative intensities of binary clusters with smaller value of y. However, for the clusters with y > 7, there are some differences.

In addition it is clear that, for the binary clusters $[CoPb_y]^-$ with y = 5, 8, 10 or 12, relative intensities of these ions are always high, presumably reflecting their higher stabilities. In contrast, the $[CoPb_{11}]^-$ binary cluster corresponds to a local intensity minimum and is presumably unstable. For the $[Co_2Pb_y]^-$ cluster series, when y is 4, 8 or 11, the relative intensities are higher, indicating that their stabilities are higher than those of other $[Co_2Pb_y]^-$ clusters.

In the experiments on lead plus cobalt, no Co/Pb binary cluster cations were observed, and the intensities of peaks for pure lead cluster cations were also very weak or not observable.

The clustering abilities between Pb and other transition metals such as Ti, Cr, Mn, Fe, Ni, Cu, Zn, Pd, and Ag, as well as the main group element Al, were also investigated. Figure 3 shows the mass spectra of anions produced by laser ablation of mixed samples of M/Pb; the data are also summarized in

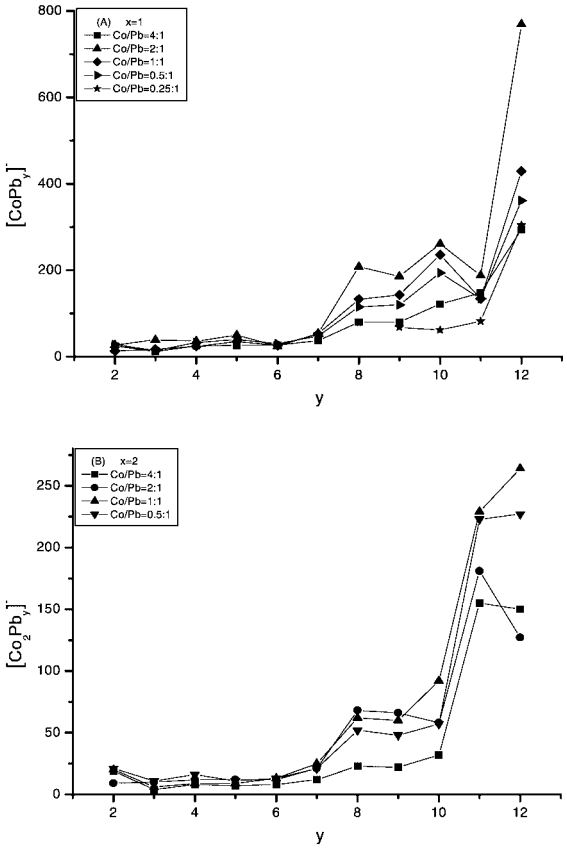

Figure 2. Relative intensities of $[CoPb_y]^-$ (A) and $[Co_2Pb_y]^-$ (B) binary alloy cluster series for different sample molar ratios. The absolute intensities of $[Pb_y]^-$ (i.e. $x = 0$) are defined as 100 in each case.

Table 1. It is clear that laser ablation of mixtures of Pb plus Ti, Mn, Fe, or Ni produces intensities of pure lead cluster anions that are the same as those produced from Co/Pb mixtures. That is, the abundances of pure $[Pb_y]^-$ clusters are still highest when the number of lead atoms $y \leq 7$, while those binary clusters containing 1–3 transition metal atoms are the second most abundant. When the number of lead atoms $y > 7$, the intensities of $[MPb_y]^-$ binary clusters are higher than those of the corresponding pure $[Pb_y]^-$ clusters. As the number of transition metal atoms increases, the intensities of the binary clusters gradually decrease.

However, for laser ablation of mixtures of Ti/Pb or Cr/Pb, the distribution of binary cluster anions is different. Only when the number of lead atoms $y = 12$ are the intensities of Ti/Pb or Cr/Pb binary clusters higher than those of the corresponding pure $[Pb_y]^-$ clusters. In addition, several oxide-containing ternary clusters Ti/Pb/O or Cr/Pb/O were observed. With an increase of the content of lead in the sample, the abundances of M/Pb/O ternary clusters also increased ($y < 7$).

For the transition metal Zn, no binary cluster anions were observed. By laser ablation of the samples with molar ratio Al/Pb = 6:1, $[Al_xPb_y]^-$ binary clusters ($x = 1$–5, $y = 1$–9) were observed; however, when the molar ratio of the sample decreases to Al/Pb = 1:1, the Al/Pb binary clusters disappear. These observations are consistent with the fact that it is generally difficult for Zn with fully filled electron shells, and main group elements, to react with the inert lead element to form binary cluster anions. The electronic structure of Al is $3s^23p^1$, i.e., one single p electron, so the clustering characteristics might be expected to be similar to those of alkali metals. In the process of clustering with lead, an Al atom is easily adsorbed to the surface of lead clusters. The physical adsorption is primarily controlled by thermodynamic factors, so these binary clusters form with difficulty under these conditions due to the thermal instability. It is striking that transition metals with abundant electrons are easily clustered with lead to form binary cluster anions.

For the data analysis, two different standards were used. One used the intensities of $[MPb_{10}]^-$ binary clusters as 100, and the other the intensities of pure $[Pb_y]^-$ clusters as 100. For purposes of comparison, the latter method can correct for the effects of lead concentration in the plasma. Table 1 gives the relative intensities of $[M_xPb_y]^-$ binary cluster anions as a function of x and y and of molar ratios in the sample. Table 1 shows that, except for $[CuPb_y]^-$, the binary cluster anions $[MPb_y]^-$ show magic characteristics at $y = 5$, 10 and 12, while at $y = 11$ the cluster stability appears to be a minimum. For the $[M_2Pb_y]^-$ cluster series, relatively intense peaks are observed at $y = 4$, 8 and 11, and for the $[M_3Pb_y]^-$ cluster series the $[M_3Pb_{10}]^-$ binary cluster is the most abundant. When the total number of atoms in $[M_xPb_y]^-$ binary clusters is equal to 13 ($x + y = 13$, $x \neq 0$), the cluster ions are predicted[13] to have an icosahedral structure.

However, for binary clusters $[CuPb_y]^-$ with $y \leq 10$, the relative intensities are always higher than that of $[CuPb_{10}]^-$, indicating that the bonding structure in the Cu/Pb binary cluster might be different from that in the other M/Pb binary cluster anions.

The analysis presented above shows that $[MPb_4]^-$ and $[MPb_5]^-$ cluster anions might be the unit building blocks of M/Pb binary clusters. The layer packing sequences of intense ('magic') cluster ions can then be proposed as follows:

$[MPb_4]^-$	$\underline{1}, 4$
$[M_2Pb_4]^-$	$\underline{1}, 4, \underline{1}$;
$[MPb_5]^-$	$\underline{1}, 5; 1, 4, \underline{1}$
$[MPb_{10}]^-$	$1, 4, \underline{1}, 4, 1; 5, \underline{1}, 5$
$[MPb_{12}]^-$	$1, 5, \underline{1}, 5, 1$
$[M_2Pb_9]^-$	$\underline{1}, 4, \underline{1}, 4, 1$
$[M_2Pb_{10}]^-$	$\underline{1}, 5, \underline{1}, 5$
$[M_2Pb_{11}]^-$	$\underline{1}, 5, \underline{1}, 5, 1$
$[M_3Pb_{10}]^-$	$\underline{1}, 5, \underline{1}, 5, \underline{1}$

(where $\underline{1}$ represents a transition metal atom, and the numbers not underlined represent lead atoms).

CONCLUSIONS

M/Pb binary cluster anions, except for Zn, are observed to contain at most four transition metal atoms, which is different from M/Ge binary clusters. Zn/Pb binary cluster ions were not observed with laser ablation. The experiments show that it is also very difficult to form Al/Pb clusters. The observed growth pattern for M/Pb binary alloy clusters is remarkably similar to that seen for metal clusters. That is, it

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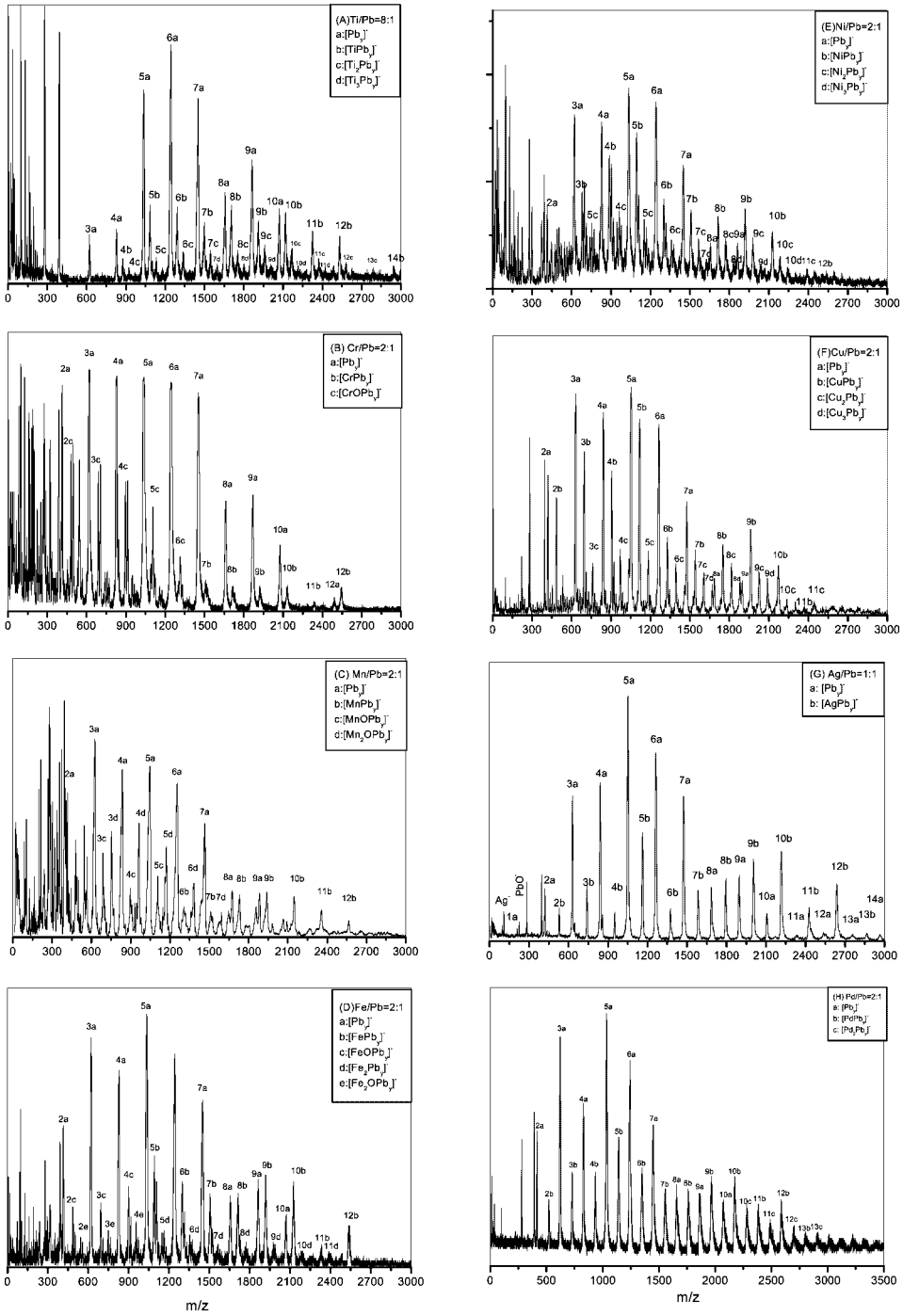

Figure 3. TOF mass spectra of $[M_xPb_y]^-$ produced by laser ablation of mixed samples of M/Pb. (Molar ratios in each sample are indicated at the top of each insert box.)

appears that transition metal atoms are sequentially attached to $[M_{x-1}Pb_y]^-$ clusters and form $[M_xPb_y]^-$ clusters by a simple condensation process. The abundance distributions (with respect to the value of y) of $[M_xPb_y]^-$ clusters are similar to those of pure $[Pb_y]^-$ clusters for most transition metals. The abundances of pure $[Pb_y]^-$ clusters are higher than those of M/Pb binary clusters with $y \leq 7$, and the abundances of the binary clusters with 1–3 transition metals are next highest. When the number of lead atoms $y > 7$, the intensities of $[MPb_y]^-$ binary clusters are higher than those of the corresponding pure $[Pb_y]^-$ clusters. As the number of transition metal atoms increases, the intensities of binary cluster anions gradually decrease.

It is proposed that $[MPb_4]^-$ and $[MPb_5]^-$ cluster anions might be the unit building blocks of M/Pb binary clusters. In addition, the layer packing sequences for magic clusters are predicted. When the total number of atoms in $[M_xPb_y]^-$ binary clusters is 13 ($x + y = 13; x \neq 0$), the cluster ions have an icosahedral structure. It is predicted that the $[MPb_{12}]^-$ binary cluster anion probably has an icosahedral structure with a

Table 1. The relative intensities of $[M_xPb_y]^-$ binary cluster anions as a function of both x and y and of molar ratios of the sample. The absolute intensities of $[Pb_y]^-$ are defined as 100 in each case

		y											
Molar ratio of M/Pb	x	2	3	4	5	6	7	8	9	10	11	12	13
Ti/Pb = 8:1	1			46	41	32	33	88	51	96	371	270	
	2			31	14	14	18	37	31	47	178	126	
	3						11	21	16	24	118	93	
Ti/Pb = 2:1	1	15	35	51	46	28	21	92	58	78	211	170	
	2	8	20	21	14	12	10	29	28	37	130		
Ti/Pb = 0.5:1	1	39	31	51	57	38	41	46	40	46	240	130	
	1	62	59	69	68	47*							
Cr/Pb = 6:1	1	59	38	41	33	18*	11	17	16	29	119	145	
Cr/Pb = 2:1	1	69	58	55	45	24*	14	23	21	39	13	168	
Mn/Pb = 6:1	1	47	28	26	16	7*	91	63	91	160	190	197	
	2	63	44	48	37	20	61*						
Mn/Pb = 2:1	1	67	43	29	4*	20	22	92	102	256	311	270	
	2	77	54	68	53	35	22*						
Fe/Pb = 6:1	1	67	52	48*	44	24	27	84	90	165	182	394	
	2	37	23	20*	10	8	9	31	25	34			
Fe/Pb = 2:1	1	42	28	41*	44	40	45	104	106	162	164	308	
	2	21	16	23*	15	15	14	36	29	32	116		
Fe/Pb = 1:1	1	84	51	63*	67	39	32	80	110	204	201	464	
	2	42	32	24*	21	15	12	29	21	48	121		
Co/Pb = 4:1	1	25	12	25	26	27	37	80	80	122	148	294	
	2	19	4	8	7	8	12	23	22	32	155	150	
	3								11	16			
Co/Pb = 2:1	1	27	39	36	50	24	54	208	186	261	188	769	
	2	9	10	12	12	12	21	68	66	58	181	127	
	3				5	5	10	35	32	50	148		
Co/Pb = 1:1	1	13	17	24	35	26	53	133	143	236	134	429	
	2	20	6	9	9	13	25	62	60	92	229	264	
	3						12	27	29	60	157	163	
	4								19	39	112	121	
Co/Pb = 0.5:1	1	28	14	33	40	30	48	115	120	194	134	361	
	2	21	11	16	11	13	21	52	48	57	223	227	
	3									29	136	129	
	4											64	
Co/Pb = 0.25:1	1								68	62	82	304	
Ni/Pb = 6:1	1	81	54	70	70	42	65	137	150	260	147	129	
	2	47	23	32	27	20	35	93	79	131	117	90	
	3						20	53	43	82			
Ni/Pb = 2:1	1	73	56	80	77	48	64	158	175	264	94	121	
	2	57	31	47	35	26	40	108	112	153	123	121	
	3						24	68	53	102	112	100	
Ni/Pb = 1:1	1	51	20	48	43	36	57	153	174	227	110	190	
	2	61	17	35	19	24	37	110	114	120	169	159	
	3						27	75	73	84	169	117	
Cu/Pb = 4:1	1	61	69	58	71	27	52	231	280	342			
	2	7	21	25	17	19	33	131	125	128			
	3							79	105				
Cu/Pb = 2:1	1	84	74	71	86	41	58	192	247	394	130		
	2	13	23	33	28	27	38	140	128	129	200		
	3						27	92	109	106			
Ag/Pb = 4:1	1	48	31	14	56	13	26	81	97	226	468	600	
Ag/Pb = 1:1	1	62	39	18	44	18	35	117	125	312	597	657	115
Pd/Pb = 2:1	1	45	38	55	32	45	51	94	127	143	281	397	196
	2									92	196	209	206
Al/Pb = 6:1	1	43	44	49	50	49	21	92	59	40			
	2	32	21	34	22	17	23	61	32				
	3	20	24	14	14	10	12	47					
	4	15	12	12	6	8	11	39					
	5	13	9	7	6								

*When the number of lead atoms y is less than or equal to the value indicated by the asterisk, the listed intensities refer to the M/Pb/O ternary cluster anions.

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small cobalt atom in the center of the $[Pb_{12}]$ cage, which corresponds to a pentagonal layer packing sequence 1, 5, 1, 5, 1, while the $[MPb_{10}]^-$ binary cluster anion might have a 1, 4, 1, 4, 1 bi-capped square antiprism structure.

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