Crystal Structures of $[K(2.2.2\text{-crypt})]_4[Pb_9Mo(CO)_3]$ − Isolation of the Novel Isomers $[(\eta^5\text{-}Pb_9)Mo(CO)_3]^{4-}$ beside $[(\eta^4\text{-}Pb_9)Mo(CO)_3]^{4-}$

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Dedicated to Prof. Dr. H. H. Karsch on the occasion of his 60th birthday

Keywords: Cluster compounds / Cryptands / Isomers / Packing / Zintl anions

The reaction of $[Mo(CO)_3(MeCN)_3]$ with K_4Pb_9 in the presence of 2.2.2-cryptand (2.2.2-crypt) has been investigated. The transition metal complex $[K(2.2.2\text{-crypt})]_4[(\eta^5\text{-}Pb_9)\text{-}Mo(CO)_3]$ (**1**), which contains a Pb_9^{4-} Zintl anion coordinated by Mo in an η5-fashion, is isolated for the first time and characterized by single-crystal X-ray structure analysis. The 10 metal atoms in the $[(\eta^5\text{-}Pb_9)Mo(CO)_3]^{4-}$ anion form a bicapped square antiprism, with the $Mo(CO)_3$ unit occupying a waist vertex position. The IR spectra of single crystals, as well as of the crude product, show clearly that only the $[(\eta^5\text{-}Pb_9)Mo(CO)_3]^{4-}$ ion is formed. In contrast, the reaction of $[Mo(CO)_3(Mes)]$ with K_4Pb_9 under the same reaction conditions gives a mixture of compound **1** and its isomer $[K(2.2.2\text{-crypt})]_4[(\eta^4\text{-}Pb_9)Mo(CO)_3]$ (**2**). Compounds **1** and **2** were isolated without additional solvent molecules. The Pb–Mo, Pb–Pb, and Mo–C bond lengths and Mo–C–O bond angles in the η4- and η5-isomers are compared and the packing of compounds **1** and **2** is discussed.
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Introduction

The chemistry of group 14 Zintl ions of the type E_9^{4-} (E = Si, Ge, Sn, Pb) is of growing interest due to the remarkable chemical reactivity of these clusters and their potential application in the preparation of ligand-free nanomaterials.[1] According to Wade's rules, an E_9^{4-} cluster adopts a discrete nine-vertex, 22-electron structure with C_{4v} point symmetry which can be described as a monocapped distorted square antiprism.[2] In the case of the Ge_9^{4-} cluster, progress has been made in the field of oxidative coupling reactions of these Zintl anions. Smaller oligomers such as the dimeric $[Ge_9\text{–}Ge_9]^{6-}$,[3] the trimeric $[Ge_9{=}Ge_9{=}Ge_9]^{6-}$,[4] and the tetrameric $[Ge_9{=}Ge_9{=}Ge_9{=}Ge_9]^{8-}$[5,6] and polymeric representatives[7] have been reported. Recently, a polymeric anion $^1_\infty[HgGe_9]^{2-}$ with Zintl ions as building blocks covalently linked by heteroatoms has been reported by our group.[8] Nucleophilic addition of $BiPh_3$ and $SbPh_3$ has also been realized in order to synthesize functionalized clusters like $[Ph_2Bi\text{–}Ge_9\text{–}BiPh_2]^{2-}$[9] and $[Ph_2Sb\text{–}Ge_9\text{–}SbPh_2]^{2-}$.[10] In the case of the Ge clusters, only one transition metal complex of the composition $[Ge_6\{Cr(CO)_5\}_6]^{2-}$ is known so far.[11]

Oxidative coupling reactions of the heavier homoatomic Sn_9^{4-} cluster have also been studied,[12] although no oligomers and polymers have been reported so far. In the case of the heavier homoatomic Sn_9^{4-} and Pb_9^{4-} Zintl clusters the research interests are mainly focused on their reaction with transition metal complexes. Although a few cases concerning the fragmentation of E_9^{4-} Zintl ions and the formation of clusters of different sizes have been reported recently,[13] in most cases the cluster ions stay intact and act as coordinating ligands to the transition metals. The resulting 10-atom heteroatomic Zintl ions are also called "metalated Zintl ions". The first NMR experiments involving the reaction of E_9^{4-} anions (E = Sn, Pb) with $[Pt(PPh_3)_4]$ in ethylenediamine (en) were described by Rudolph in 1983.[14] However, up to now only a few structurally characterized metalated Zintl ions have been reported, most of which are polystannide complexes, including $[Sn_9M(CO)_3]^{4-}$ (M = Cr, Mo, W),[15–17] $[Sn_9Pt_2(PPh_3)]^{2-}$,[18] and $[Sn_9Ni_2(CO)]^{3-}$.[18] Although the first synthesis of the Pb_9^{4-} Zintl ion by Joannis dates back to 1891,[19] and several important synthetic routes for the preparation of Pb_9^{4-} have been developed since then,[20] the reaction of Pb_9^{4-} with transition metal complexes has remained almost unexplored, and only three metalated complexes of the composition $[Pb_9M(CO)_3]^{4-}$ (M = Cr, Mo, W) have been reported.[16,21] It is worth pointing out that the $[Pb_9Mo(CO)_3]^{4-}$ ion has been characterized in the salt $Mo(CO)_3(en)_2[K(2.2.2\text{-crypt})]_4[Pb_9Mo(CO)_3]\cdot 2.5en$ (**3**), although it could not be obtained without $Mo(CO)_3(en)_2$.[16] In the reported complexes the ML_n fragment usually resides in a capping position, with the *nido*-E_9^{4-} ion

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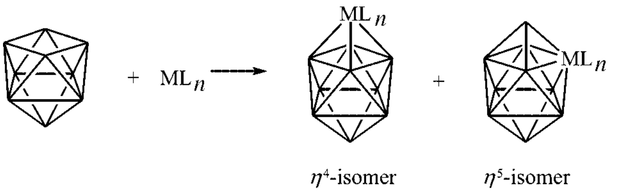
bound to the metal atom in an η^4-coordinative fashion (Scheme 1).



Scheme 1.

Recently, Eichhorn has reported an η^5-coordinated Zintl ion $[Sn_9W(CO)_3]^{4-}$, in which the $W(CO)_3$ unit occupies a waist vertex rather than sitting in a capping position.[17] The obtained product turned out to be a mixture of the η^5- and η^4-isomers in a ratio of 2:1. Metalated Sn_9^{4-} analogs of Ge_9^{4-} and Pb_9^{4-} acting as an η^5-ligand to a transition metal are still unknown. $[M(CO)_3(Mes)]$ (M = Cr, Mo, W) complexes are the most frequently used organometallic complexes for the reaction with E_9^{4-} Zintl ions, whereas their reaction with $[M(CO)_3(MeCN)_3]$ is still unexplored to the best of our knowledge. Herein we report the reaction of K_4Pb_9 with $[Mo(CO)_3(MeCN)_3]$ and the isolation of the first representative of a metalated η^5-Pb_9^{4-} Zintl ion in the solvate-free compound [K(2.2.2-crypt)]$_4$[(η^5-Pb$_9$)Mo(CO)$_3$] (**1**), where 2.2.2-crypt stands for 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane. According to the results of IR and X-ray analyses, the reaction affords exclusively the η^5-isomer. The reaction of K_4Pb_9 with $[Mo(CO)_3(Mes)]$ was also reinvestigated under the same reaction conditions. In contrast to the previous report,[16] we observed the formation of compound **1** together with its η^4-isomer [K(2.2.2-crypt)]$_4$[(η^4-Pb$_9$)Mo(CO)$_3$] (**2**).

[K(2.2.2-crypt)]$_4$[(η^5-Pb$_9$)Mo(CO)$_3$] (**1**)

[K(2.2.2-crypt)]$_4$[(η^4-Pb$_9$)Mo(CO)$_3$] (**2**)

Mo(CO)$_3$(en)$_2$[K(2.2.2-crypt)]$_4$[(η^4-Pb$_9$)Mo(CO)$_3$]·2.5en (**3**)

K$_2$[K(2.2-crypt)]$_2$[Pb$_5${Mo(CO)$_3$}$_2$](en)$_3$ (**4**)

Results and Discussion

Synthesis of Compounds 1 and 2

[K(2.2.2-crypt)]$_4$[(η^5-Pb$_9$)Mo(CO)$_3$] (**1**) was prepared by the slow addition of a toluene solution of [Mo(CO)$_3$(MeCN)$_3$][22] to a solution of K_4Pb_9 in ethylenediamine (en) in the presence of 4 equiv. of 2.2.2-crypt. Within 2 h the color of the resulting reaction mixture changed from deep grey to deep reddish-brown. After careful layering with toluene, single crystals of compound **1** started to grow on the walls of the vessel and became visible within a few hours. After one week the solution became colorless, indicating the completeness of the crystallization. Black crystals suitable for single-crystal X-ray diffraction studies were obtained. No additional phases were formed, since the unit cells of several crystals of compound **1** were checked by X-ray diffraction and all of them turned out to be the η^5-complex.

The reaction of K_4Pb_9 with $[Mo(CO)_3(Mes)]$ under the same reaction conditions afforded an isomeric mixture of [K(2.2.2-crypt)]$_4$[(η^4-Pb$_9$)Mo(CO)$_3$] (**2**) and [K(2.2.2-crypt)]$_4$[(η^5-Pb$_9$)Mo(CO)$_3$] (**1**). Surprisingly, compound **2** obtained under these reaction conditions is solvate-free and does not contain an additional $Mo(CO)_3$ fragment as reported for compound **3**.[16] Repetition of the reaction led to variable ratios of the two isomers.

Crystal Structure Analyses of Compounds 1 and 2

Compound 1

The crystal structure analysis of compound **1** shows that the unit cell contains two [(η^5-Pb$_9$)Mo(CO)$_3$]$^{4-}$ anions and eight [K(2.2.2-crypt)]$^+$ cations. Four 2.2.2-crypt-coordinated K^+ cations per cluster clearly indicate a charge allocation of –4 for the 10-atom heteroatomic polyanion. Four [K(2.2.2-crypt)]$^+$ units surround the cluster unit at a distance where interionic interactions can be excluded. The shortest Pb–K distance is 7.195 Å. During the refinement, relatively large difference Fourier peaks were located near the Pb atoms, indicating a disorder of the anions which could be resolved by applying a split model (ratio 0.85:0.15). A very similar disorder, even as far as the ratio of occupation is concerned, has been observed for [(η^5-Sn$_9$)Mo(CO)$_3$]$^{4-}$.

As emphasized in Figure 1, the [(η^5-Pb$_9$)Mo(CO)$_3$]$^{4-}$ ion forms a bicapped square antiprism. The most important feature of this polyhedron is that the $Mo(CO)_3$ unit occupies a waist vertex. This *closo* antiprism is built up by a bottom square plane (Pb2–Pb5), a top square plane (Pb6–Pb8 and Mo), and two capping atoms (Pb1, Pb9). The data of the crystal structure determination of compound **1** are listed in the Exp. Sect., and selected bond lengths and angles for [(η^5-Pb$_9$)Mo(CO)$_3$]$^{4-}$ are given in Table 1. The Mo–Pb bond lengths in [(η^5-Pb$_9$)Mo(CO)$_3$]$^{4-}$ are different (Table 1), with the contacts of the Mo atom to the apical Pb9 atom and to the Pb2 and Pb5 atoms of the bottom square being remarkably shorter (2.962–3.063 Å) than those to the atoms Pb6 and Pb8 of the top square plane (3.220–3.241 Å). Since these two longer Mo–Pb distances are comparable to the two Pb–Pb contacts within the top square plane (3.278–3.285 Å), the whole cluster can be regarded as regularly shaped, even though the $Mo(CO)_3$ unit is in a waist position. Due to the higher coordination number of the Mo atom in [(η^5-Pb$_9$)Mo(CO)$_3$]$^{4-}$, the mean Mo–Pb distance of 3.1074 Å is slightly longer than that in the η^4-isomers (3.028 and 3.032 Å) in compounds **2** and **3**[16] (Table 2). This distance is also significantly longer than the sum of the covalent radii of the metals involved (2.834 Å).[23] The Pb–Pb distances within the top plane are approximately 0.2 Å longer than those in the bottom plane. However, the angles within the bottom plane (90.0 ± 0.9°) lie within a narrower range than those in the top plane (90.0 ± 2.9°). Similar to the different W–C distances in the related η^5- and η^4-[(Sn$_9$)W(CO)$_3$]$^{4-}$ complexes, the corresponding Mo–C distances in [(η^5-Pb$_9$)Mo(CO)$_3$]$^{4-}$ are longer (1.90 Å) than those in the η^4-isomer (1.88 Å). The C–O bonds in $[(\eta^5\text{-}Pb_9)Mo(CO)_3]^{4-}$ are in the range from 1.22 to 1.23 Å and are therefore shorter than those in $[(\eta^4\text{-}Pb_9)Mo(CO)_3]^{4-}$ (1.22–1.27 Å). The Mo–C–O bond angles in $[(\eta^5\text{-}Pb_9)Mo(CO)_3]^{4-}$ deviate strongly from linearity and range from 167 to 171°, which is in contrast to other carbonyl-containing E_9^{4-} moieties like $[(\eta^5\text{-}Sn_9)W(CO)_3]^{4-}$[17] and $[(\eta^4\text{-}Pb_9)Mo(CO)_3]^{4-}$,[16] and also to $[Mo(CO)_3(Mes)]$.[21]

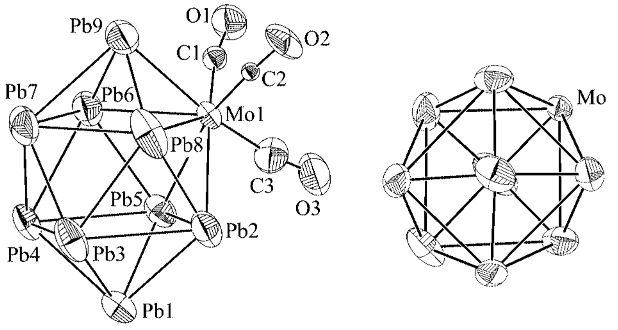


Figure 1. Molecular structure of the *closo*-$[(\eta^5\text{-}Pb_9)Mo(CO)_3]^{4-}$ unit in compound **1** (thermal ellipsoids set at 80% probability).

Table 1. Selected bond lengths [Å] and angles [°] for the $[(\eta^5\text{-}Pb_9)Mo(CO)_3]^{4-}$ unit in compound **1**.

Mo1–Pb2	3.063(1)	Pb4–Pb5	3.390(1)
Mo1–Pb5	3.051(1)	Pb4–Pb6	3.186(1)
Mo1–Pb6	3.220(1)	Pb4–Pb7	3.070(1)
Mo1–Pb8	3.241(1)	Pb5–Pb6	3.011(1)
Mo1–Pb9	2.962(1)	Pb6–Pb7	3.278(1)
Pb1–Pb2	3.069(1)	Pb6–Pb9	3.026(1)
Pb1–Pb3	3.055(1)	Pb7–Pb8	3.285(1)
Pb1–Pb4	3.060(1)	Pb7–Pb9	3.198(1)
Pb1–Pb5	3.070(1)	Pb8–Pb9	3.034(1)
Pb2–Pb3	3.415(1)	Mo1–C1	1.92(1)
Pb2–Pb5	3.272(1)	Mo1–C2	1.89(1)
Pb2–Pb8	3.038(1)	Mo1–C3	1.89(2)
Pb3–Pb4	3.211(1)	C1–O1	1.22(2)
Pb3–Pb7	3.100(1)	C2–O2	1.22(2)
Pb3–Pb8	3.157(1)	C3–O3	1.23(2)
O1–C1–Mo1	167(1)	C1–Mo1–C2	91.9(6)
O2–C2–Mo1	167(1)	C1–Mo1–C3	93.1(6)
O3–C3–Mo1	171(1)	C2–Mo1–C3	95.6(6)
Pb5–Mo1–Pb9	112.38(4)	Pb2–Pb1–Pb4	100.35(2)
Pb2–Mo1–Pb9	112.82(4)	Pb3–Pb1–Pb5	99.96(2)
Pb2–Mo1–Pb6	102.57(3)	Mo1–Pb9–Pb7	99.02(3)
Pb5–Mo1–Pb8	101.72(3)	Pb6–Pb9–Pb8	96.47(2)
Pb6–Mo1–Pb8	88.79(3)	Pb3–Pb2–Pb5	89.07(2)
Mo1–Pb6–Pb7	92.33(3)	Pb2–Pb3–Pb4	90.49(2)
Pb6–Pb7–Pb8	87.05(2)	Pb3–Pb4–Pb5	90.54(2)
Mo1–Pb8–Pb7	91.82(3)	Pb2–Pb5–Pb4	89.90(2)

Table 2. Structural comparison of the anions in compounds **1**, **2**, and **3**.

	1[a]	2[a]	3[b]
Mean *d*(Pb1 to Pb2, 3, 4, 5) [Å]	3.064	3.074	3.048
Mean *d*(Pb–Pb) in bottom plane [Å][c]	3.322	3.320	3.319
Mean *d*(Pb–Pb/Pb–Mo) in top plane [Å]	3.256	3.202	3.207
Mean *d*(Mo–Pb) [Å]	3.107	3.028	3.032
Mean *d*(Mo–C) [Å]	1.90	1.88	1.93
Mean *d*(C–O) [Å]	1.22	1.23	1.18
Mean Mo–C–O [°]	168	172	178

[a] This work. [b] Ref.[16] [c] The square plane containing the atoms Pb2, Pb3, Pb4, and Pb5 is defined as the bottom plane; the other square plane in the 10-atom polyhedra is defined as the top plane.

Compound 2

The crystal structure analysis of compound **2** shows that the unit cell contains four $[(\eta^4\text{-}Pb_9)Mo(CO)_3]^{4-}$ anions and sixteen $[K(2.2.2\text{-crypt})]^+$ cations. Four 2.2.2-crypt-bound K^+ cations per cluster allow the clear charge allocation of –4 for the 10-atom heteroatomic polyanion. As observed in compound **1**, the four $[K(2.2.2\text{-crypt})]^+$ units in compound **2** are at a large distance from the polyanion and show no coordination to the cluster anion. The distances between the K^+ cations and the polyanions are longer than 7.37 Å. Due to the poor quality of the crystals the reflex intensities were low, and during the refinement relatively large difference Fourier peaks were located near the Pb atoms, indicating a disorder of the anions. Attempts to resolve the disorder were not successful.

As shown in Figure 2, the metal atoms of the $[(\eta^4\text{-}Pb_9)Mo(CO)_3]^{4-}$ ion again form a bicapped square antiprism, but this time with the $Mo(CO)_3$ unit in a capping position. The *closo* antiprism is built up by a bottom square plane (Pb2–Pb5), a top square plane (Pb6–Pb9), and two capping atoms (Pb1, Mo). The data of the crystal structure determination of compound **2** are listed in the Exp. Sect., and selected bond lengths and angles for the $[(\eta^4\text{-}Pb_9)Mo(CO)_3]^{4-}$ anion are given in Table 3. The contacts between the Mo atom and Pb6, Pb7, Pb8, and Pb9 of the top square plane are in the narrow range between 3.014 and 3.048 Å (average 3.028 Å), and are shorter than those observed in compounds **1** (average 3.107 Å) and **3** (average 3.032 Å). The Pb–Pb distances within the top plane range from 3.180 to 3.222 Å and are shorter than those within the bottom plane (3.249–3.428 Å). The Pb–Pb distances between the apical Pb1 and Pb2, Pb3, Pb4, and Pb5 of the bottom plane lie between 3.048 and 3.089 Å (average 3.074 Å) and are longer than those in compounds **1** (average 3.064 Å) and **3** (average 3.048 Å). The two planes have similar dimensions, which gives rise to a more regularly shaped 10-atom cluster than that observed in compounds **1** and **3**. The Pb–Pb distances within the top plane are approximately 0.122 Å shorter than those within the bottom plane. However, the angles within the top plane (90.0 ± 0.9°) lie within a narrower range than those within the bottom plane (90.0 ± 1.9°). In this respect, compound **2** is quite different from compounds **1** and **3**.

Although compounds **2** and **3** contain the same polyhedral core of 10 atoms, the Mo–C–O bond angles in these two compounds are significantly different (Table 2). The mean Mo–C–O bond angle (178°) in compound **3** is almost linear, whereas the corresponding angle in compound **2** deviates strongly from linearity (172°). As shown in Table 2, the Pb–Pb bond lengths within the bottom planes are almost identical (3.322 vs. 3.320 Å) despite the different location of the $Mo(CO)_3$ fragment. The elongation of the mean Mo–Pb distance in the η^5-isomer is a consequence of the higher coordination number. The two elongated bonds

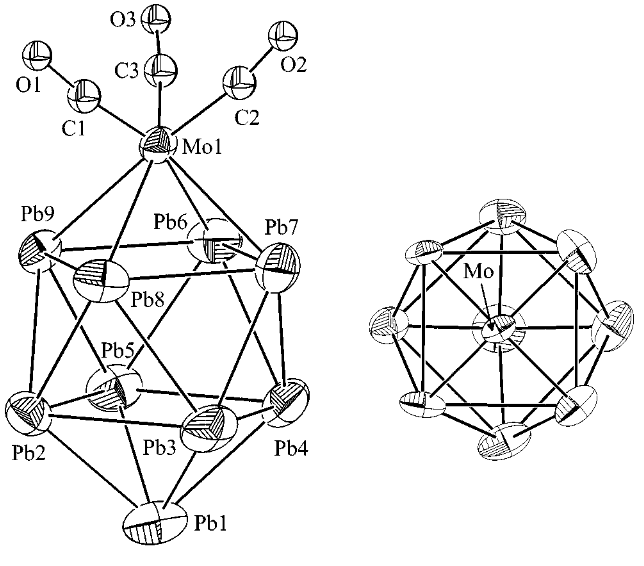


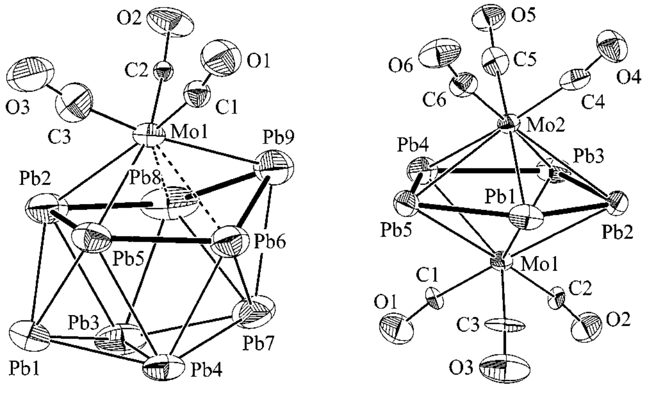
Figure 2. Molecular structure of the *closo*-$[(\eta^4\text{-}Pb_9)Mo(CO)_3]^{4-}$ unit in compound **2** (thermal ellipsoids set at 50% probability).

Table 3. Selected bond lengths [Å] and angles [°] for the $[(\eta^4\text{-}Pb_9)\text{-}Mo(CO)_3]^{4-}$ unit in compound **2**.

Mo1–Pb6	3.030(5)	Pb4–Pb5	3.249(3)
Mo1–Pb7	3.017(4)	Pb4–Pb6	3.137(3)
Mo1–Pb8	3.048(4)	Pb4–Pb7	3.207(3)
Mo1–Pb9	3.014(4)	Pb5–Pb6	3.115(3)
Pb1–Pb2	3.048(3)	Pb5–Pb9	3.138(3)
Pb1–Pb3	3.087(3)	Pb6–Pb7	3.222(3)
Pb1–Pb4	3.089(3)	Pb6–Pb9	3.192(2)
Pb1–Pb5	3.072(3)	Pb7–Pb8	3.215(3)
Pb2–Pb3	3.428(3)	Pb8–Pb9	3.180(2)
Pb2–Pb5	3.293(3)	Mo1–C1	1.83(5)
Pb2–Pb8	3.100(3)	Mo1–C2	1.90(5)
Pb2–Pb9	3.063(3)	Mo1–C3	1.92(5)
Pb3–Pb4	3.309(3)	C1–O1	1.27(5)
Pb3–Pb7	3.100(3)	C2–O2	1.21(5)
Pb3–Pb8	3.149(3)	C3–O3	1.21(5)
O1–C1–Mo1	173(4)	C1–Mo1–C2	92(2)
O2–C2–Mo1	171(4)	C1–Mo1–C3	98(2)
O3–C3–Mo1	172(4)	C2–Mo1–C3	84(2)
Pb7–Mo1–Pb9	97.0(1)	Pb2–Pb1–Pb4	99.53(8)
Pb6–Mo1–Pb8	96.7(1)	Pb3–Pb1–Pb5	99.56(9)
Pb3–Pb2–Pb5	88.79(6)	Pb7–Pb6–Pb9	89.53(6)
Pb2–Pb3–Pb4	88.11(6)	Pb6–Pb7–Pb8	89.71(6)
Pb3–Pb4–Pb5	91.63(7)	Pb7–Pb8–Pb9	89.87(6)
Pb2–Pb5–Pb4	91.47(7)	Pb6–Pb9–Pb8	90.87(6)

(Mo–Pb6, Mo–Pb8) originate from the nonplanarity of the five coordinated Pb atoms.

Very recently, another compound of the composition $K_2[K(2.2\text{-crypt})]_2[Pb_5\{Mo(CO)_3\}_2](en)_3$ (**4**) with Mo–Pb and Pb–Pb bonds has been reported by our group.[24] The structure of the $[\{(OC)_3Mo\}Pb_5\{Mo(CO)_3\}]^{4-}$ anion (Figure 3b) contains a planar five-membered ring of lead atoms. The Pb–Pb bond lengths between 3.014(1) and 3.065(1) Å (average 3.041 Å) in compound **4** are significantly shorter than those in compounds **1** and **2** (d_{Pb-Pb} = 3.011–3.415 Å and 3.048–3.428 Å, respectively). Interestingly, the Mo–Pb distances (3.014–3.048 Å) in compound **2** are very similar to those in compound **4** (3.001–3.093 Å), but differ from those in compound **1** (2.962–3.241 Å). Compound **1** can be regarded as an intermediate in the fragmentation of the Pb_9^{4-} cluster and the formation of the novel Pb_5 cluster fragment in **4** (Figure 3).



(a) (b)

Figure 3. (a) Molecular structure of the *closo*-$[(\eta^5\text{-}Pb_9)Mo(CO)_3]^{4-}$ unit in compound **1** (thermal ellipsoids set at 80% probability) (dotted lines represent Mo–Pb distances >3.2 Å). (b) The structure of the *closo*-$[\eta^5\text{-}Pb_5\{Mo(CO)_3\}_2]^{4-}$ Zintl anion (thermal ellipsoids set at 80% probability).

Cluster Arrangements

The packing diagrams of compounds **1** and **2** are shown in Figures 4 and 5, respectively. Both compounds form distorted hexagonal layers. The distances between the cluster units within the same layers differ by less than 10% (distance range for **1** from 15.465 to 16.774 Å and for **2** from 15.066 to 16.477 Å). In compound **1** the interlayer distances between the centers of gravity of the clusters are 15.493, 15.853 (2×), and 15.144 Å. The orientation of the $M(CO)_3$ groups with respect to the layers has no significant influence on the distances between the clusters. Irrespective of their orientation the two different layers of clusters (I and II), one of which is shown in Figure 4a, arrange in a cubic-type packing as indicated in Figure 4b by the labels ABCA perpendicular to the *ab* plane (not along *c*).

In compound **2**, the distorted layers are packed pairwise along the *b* direction of the unit cell. Within the AA′ and BB′ layers (Figure 5) the $M(CO)_3$ groups of two layers are oriented towards each other, leading to a larger distance of 14.431 Å between these layers as compared to the A′B and B′A interlayer distance of 12.502 Å. Consequently, different intercluster distances of 16.617 and 14.308 Å occur. The relative orientation of the carbonyl groups of the $Mo(CO)_3$ unit might be the origin of the larger unit cell volume of **2** if compared to **1**.

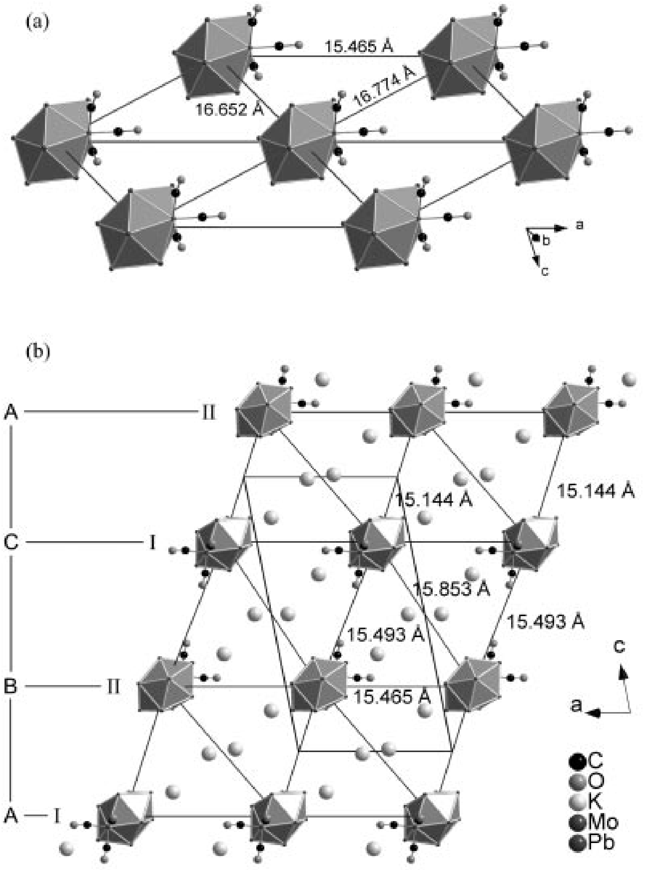


Figure 4. (a) The hexagonal packing in the *ab* plane in the single crystal of compound **1**. (b) The stacking sequence of the layers along the *c* axis in compound **1** (2.2.2-crypt units are not shown).

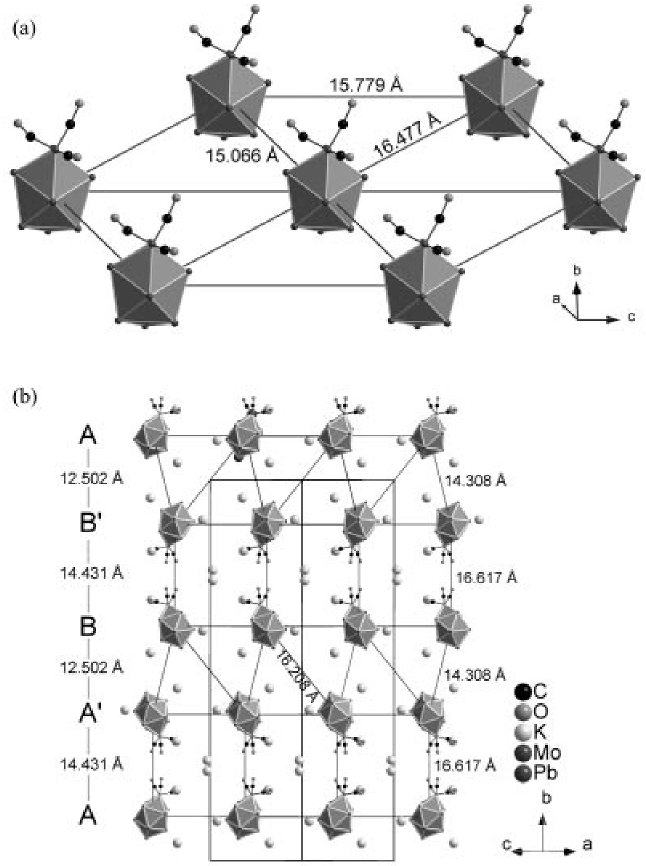


Figure 5. (a) The hexagonal packing in the *ac* plane in the single crystal of compound **2**. (b) The stacking sequence of the layers along the *b* axis in compound **2** (2.2.2-crypt units are not shown).

IR Spectra

Single crystals of **1** and the crude product were carefully checked by solid-state IR analyses. The characteristic CO stretching vibrations of the η^5-isomer are found at 1809 and 1697 cm^{-1}. None of the characteristic peaks of the η^4-isomer ($\tilde{\nu}$ = 1813, 1736, and 1702 cm^{-1})[16] were detected (Table 4). The carbonyl bands of the η^5-isomer are red-shifted relative to those of the η^4-isomer. This red-shift has also been observed for the isomeric compounds [(η^5-Sn$_9$)-W(CO)$_3$]$^{4-}$ ($\tilde{\nu}$ = 1805, 1701 cm^{-1}) and [(η^4-Sn$_9$)W(CO)$_3$]$^{4-}$ ($\tilde{\nu}$ = 1822, 1711, 1701 cm^{-1}; see also Table 4).

As already mentioned above, several crystals of compound **1** were checked by X-ray diffraction and identified as the η^5-isomer. The IR study gave further evidence that the reaction of [Mo(CO)$_3$(MeCN)$_3$] with K$_4$Pb$_9$ yields exclusively one isomer (**1**). Our attempts to obtain a ^{207}Pb NMR spectrum of compound **1** were unsuccessful due to its poor solubility in the usual solvents (en, DMF, THF, DMSO, and toluene).

Conclusions

The reaction of [Mo(CO)$_3$(MeCN)$_3$] with K$_4$Pb$_9$ in the presence of 2.2.2-crypt was investigated. A metalated Zintl ion [K(2.2.2-crypt)]$_4$[(η^5-Pb$_9$)Mo(CO)$_3$] (**1**) was isolated and characterized by single-crystal X-ray structure and IR analyses. The carbonyl (CO) stretching vibrations ($\tilde{\nu}$ = 1807, 1697 cm^{-1}) in the IR spectrum of compound **1** clearly show the exclusive formation of the [(η^5-Pb$_9$)Mo(CO)$_3$]$^{4-}$ isomer. The [K(2.2.2-crypt)]$_4$[(η^4-Pb$_9$)Mo(CO)$_3$] isomer (**2**), which has been isolated for the first time as a pure product, is formed together with its isomer **1** in the reaction of [Mo(CO)$_3$(Mes)] with K$_4$Pb$_9$ under the same reaction conditions.

Experimental Section

The synthesis of compound **1** was carried out under argon in a glove-box or in a Schlenk line. The IR spectra were recorded from KBr pellets with a JASCO FT/IR-460 spectrometer. The X-ray crystal data were collected with a Nonius Kappa CCD device at the window of a rotating anode X-ray generator and processed with the SHELXS-97 and SHELXL-97 program packages.[25] The crystallographic data for the structures are summarized in Table 5. CCDC-258685 (**1**) and -258686 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The elemental analyses were carried out by the Microanalytical Laboratory at TU Munich. Toluene (Merck) and en (Merck) were dried with K/CaH$_2$ (Fluka),

Table 4. The characteristic CO stretching vibrations in E_9 Zintl complexes.

Complexes	ν_{CO} [cm^{-1}]	Ref.
$[K(2.2.2\text{-crypt})]_4[(\eta^4\text{-}Sn_9)Cr(CO)_3]$	1822, 1705	[17]
$[K(2.2.2\text{-crypt})]_4[(\eta^4\text{-}Sn_9)Mo(CO)_3]$	1829, 1708	[17]
$[K(2.2.2\text{-crypt})]_4[(\eta^4\text{-}Sn_9)Mo(CO)_3]$	1830, 1718, 1703	[16]
$[K(2.2.2\text{-crypt})]_4[(\eta^5\text{-}Sn_9)W(CO)_3]$	1805, 1701	[17]
$[K(2.2.2\text{-crypt})]_4[(\eta^4\text{-}Sn_9)W(CO)_3]$	1822, 1711, 1701	[16]
$[K(2.2.2\text{-crypt})]_4[(\eta^4\text{-}Pb_9)Cr(CO)_3]$	1791, 1695, 1681	[21]
$Mo(CO)_3(en)_2[K(2.2.2\text{-crypt})]_4[(\eta^4\text{-}Pb_9)Mo(CO)_3]$	1813, 1736, 1702	[16]
$W(CO)_3(en)_2[K(2.2.2\text{-crypt})]_4[(\eta^4\text{-}Pb_9)W(CO)_3]$	1804, 1697, 1686	[16]
$[K(2.2.2\text{-crypt})]_4[(\eta^5\text{-}Pb_9)Mo(CO)_3]$	1809, 1697	this work
$K_2[K(2.2\text{-crypt})]_2[Pb_5\{Mo(CO)_3\}_2](en)_3$	1889, 1878, 1737	[24]

Table 5. Crystallographic data for compounds **1** and **2**.

	$[K(2.2.2\text{-crypt})]_4[(\eta^5\text{-}Pb_9)Mo(CO)_3]$	$[K(2.2.2\text{-crypt})]_4[(\eta^4\text{-}Pb_9)Mo(CO)_3]$
Empirical formula	$C_{75}H_{144}K_4Mo_1N_8O_{27}Pb_9$	$C_{75}H_{144}K_4MoN_8O_{27}Pb_9$
Formula mass [g mol^{-1}]	3707.03	3707.03
Temperature [K]	173(2)	120(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (no.2)	$P2_1/n$ (no. 14)
a [Å]	15.4651(1)	15.066(1)
b [Å]	16.6519(1)	53.866(1)
c [Å]	25.5701(2)	15.779(1)
α [°]	79.265(1)	90
β [°]	75.144(1)	115.473(1)
γ [°]	62.842(1)	90
Volume [Å³]	5644.9(1)	11560.7(3)
Z	2	4
$\rho_{calcd.}$ [g cm^{-3}]	2.181	2.130
μ [mm^{-1}]	13.686	13.366
$F(000)$	3444	6888
Crystal size [mm]	0.40 × 0.40 × 0.20	0.20 × 0.10 × 0.05
θ range [°]	1.38 to 25.37	4.09 to 20.85
Index ranges	$0 \le h \le 18$	$-15 \le h \le 13$
	$-17 \le k \le 20$	$0 \le k \le 37$
	$-29 \le l \le 30$	$0 \le l \le 15$
Reflections collected	126980	49478
Independent reflections	20659 (R_{int} = 0.084)	9540 (R_{int} = 0.180)
Goodness-of-fit on F^2	1.067	1.021
Final R indices[$I > 2\sigma(I)$]	R_1 = 0.058, wR_2 = 0.137	R_1 = 0.103, wR_2 = 0.257
R indices (all data)	R_1 = 0.082, wR_2 = 0.148	R_1 = 0.148, wR_2 = 0.287
Largest peak/hole [e Å^{-3}]	3.107/–2.146	8.597/–3.409

freshly distilled, and degassed. The binary phase of the formal composition "K_4Pb_9" was prepared by a high-temperature reaction (350 °C) from the elements K and Pb in the ratio of 4:9. Tricarbonyl(mesitylene)molybdenum and tris(acetonitrile)tricarbonylmolybdenum were prepared by heating $Mo(CO)_6$ (Alfa Inorganics) in an excess of mesitylene or MeCN under reflux under nitrogen according to the reported methods.[22]

K_4Pb_9 (100 mg, 0.049 mmol) and 2.2.2-crypt (74 mg, 0.2 mmol) were dissolved in en (ca. 1 mL) and stirred for 5 min. A yellow solution of $[Mo(CO)_3(MeCN)_3]$ (16 mg, 0.051 mmol) in toluene (ca. 2 mL) was then added to the green solution of K_4Pb_9. The resulting mixture was stirred at room temperature for another 2 h. After filtration, the filtrate was layered with toluene (2 mL). Within 48 h, dark-brown crystals of $[K(2.2.2\text{-crypt})]_4[Pb_9Mo(CO)_3]$ precipitated (48 mg, ca. 45% with respect to K_4Pb_9). Elemental analysis of the products from this reaction (3707.03): calcd. C 24.30, H 3.92, N 3.02; found C 24.49, H 3.60, N 3.18. The reaction of K_4Pb_9 (100 mg, 0.049 mmol) with $[Mo(CO)_3(Mes)]$ (15 mg, 0.049 mmol) was carried out under the same reaction conditions with the same workup procedure.

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