On the Instability of Iodides of Heavy Main Group Atoms in their Higher Oxidation State

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ABSTRACT: Inert pair effect—the tendency of s orbital of heavy atoms to stay unreactive, is a consequence of relativistic contraction of the s orbitals. While the manifestations of this, on the reactivity depends on the nature of the substituents, this aspect is often overlooked. Divalent Pb prefers inorganic substituents, whereas tetravalent Pb prefers organic substituents. Among the inorganic substituents, again there are specific preferences—tetravalent Pb prefers F and Cl more than Br and I. It is as though the relativistic contraction of s orbital of Pb is more significant with Br and I substituents, than with Cl, F and alkyl substituents. Herein, we address the problem using molecular orbital approach. We explain why typical hypervalent systems, like 12-X-6, 10-X-5 (X is a heavy atom, the number preceding X is the number of valence electrons surrounding X, and the number after X is the coordination number) with less electronegative substituents carrying lone pair (such as Iodine), and Lewis octet molecules like PbI₄ are unstable, but their dianions (14-X-6, 12-X-5, PbI₄²⁻) are not. For heavy atoms, the relativistic contraction of s orbital renders the antibonding combination of s with ligand orbitals (σ_1^*) very low-lying, making it a good acceptor of electrons. Thus compounds where σ_1^* is empty are kinetically unstable, when an electron donor with appropriate energy (such as lone pair on Iodine or bromine) is present in the vicinity. Donor-acceptor interaction between σ_1^* and the lone pair on I or Br (F and Cl lone pairs are energetically far away from σ_1^*) is responsible for the instability of such compounds. The kinetic stability of tetraalkyl lead compounds is due to the absence of lone pairs on the alkyl substituents. This work illustrates the key factor responsible for the instability of heavy element iodides and provides a molecularlevel insight on extended solid-state structures via quasi-relativistic density functional computations.

INTRODUCTION

Why Pb forms stable tetravalent compounds with organic substituents but not with inorganic?¹ This question was addressed by Prof. Schleyer and Prof. Martin Kaupp in 1993.² They proposed that the electronegative substituents tend to destabilize the bonds in tetravalent Pb. The large positive charge on Pb due to electronegative substituents shrinks the 6s orbital which is already contracted relative to 6p, because of relativistic effect.^{3,4,5} Thus the electronegative substituents make the 6s essentially an inert pair, not participating in the bonding. This weakens the bonds in PbX₄. However, there are some ambiguities with this explanation. The study considered only H, methyl, F and Cl as substituents. The instability of PbBr₄ and PbI₄ poses a question to the above explanation.

As Br and I are less electronegative than F and Cl, PbBr₄ and PbI₄ are expected to be stable, but they are not. The widely believed explanation is that I⁻ and Br⁻ are strong reducing agents and reduces Pb(IV) to Pb(II).⁶ This explanation assumes that PbI₄ is completely ionic, and exists as Pb⁴⁺ and 4 I^{-,7} However, such may be the case for PbF₄, where the electronegativity difference is very high (1.65). The Pauling electronegativity difference between Pb and I is only 0.33. Assuming a completely ionic lattice, relative thermodynamic stabilities of higher and lower oxidation states are shown to vary depending on the size of the anion— higher oxidation state favors smaller anions, and lower oxidation state prefer larger anions.⁷ Indeed the stability of PbX₄ follows this order, however, assuming complete ionic nature is a large approximation when the atoms involved do not differ much in electronegativity. Here we are seeking for an explanation that also take into account the covalent nature of bonds.

The absence of PbI₄ and PbBr₄ crystal structures experimentally suggests a reduction reaction leading to the decomposition of PbI₄ to PbI₂ and I₂ and PbBr₄ to PbBr₂ and Br₂.^{6,8} We need to know, the mechanism of this reaction and the activation energy in order to understand the reason for the instability of PbI₄ and PbBr₄. We also realized that there are many other inorganic compounds which are unknown, such as TeI₆, TeBr₆, TeCl₆, BiI₅, SbI₅ etc..⁹ These are hypervalent structures, and hypervalent structures are known to be stable with electronegative substituents.¹⁰ If the substituents are less electronegative, the substituent-centered occupied non-bonding MOs will be high in energy, and hence would easily give off electrons.¹⁰ However, this does not explain the stability of Te(CH₃)₆, Sb(CH₃)₅, sulfuranes, persulfuranes etc. cannot be explained based on electronegativity of substituents.¹⁵ In this work, we have studied the reasons for the instability of some inorganic compounds, particularly, the iodides.

RESULTS AND DISCUSSION

Experimentally, PbI₄ is unknown, whereas PbI₂ is known and stable. The structure of PbI₂ (P-3-m1 space group) is shown in Fig. 1.²⁰⁻²¹ It is made up of PbI₆ octahedra, where each I is tricoordinated, or shared by three Pb atoms. *Conversely, if PbI₂ solid state structure is to be made up of hexacoordinate Pb atoms, for the stoichiometry to be same as PbI₂, each I should be shared by 3 Pb atoms, so that one Pb gets a total of (1/3)*6 = 2 I atoms. Similarly for BiI₃: If the solid state structure is made up of hexacoordinate Bi, each I should be shared between 2 Bi atoms, to make a total of (1/2)*6 = 3 I atoms per Bi. The structure of BiI₃ is shown in Fig.1, and it is evident that each I is*

shared by 2 Bi atoms.²² This reasoning would enable us to predict the possible structures of PbI₄. One would normally expect that PbI₄ would be a molecular crystal made up of tetrahedral molecules. However, since BiI₃, (which we would have predicted to be molecular crystal made up of trigonal pyramidal molecules) contrary to our basic chemistry knowledge is existing as an extended solid, one should consider other structural possibilities also for PbI₄.



Figure 1. Experimental structures of BiI₃ (space group P3) and PbI₂ (space group P-3-m1). The green, purple and black colored spheres indicate Bi, I and Pb atoms respectively.

If we assume that the solid state structure of PbI₄ consist of hexacoordinate Pb, then four I atoms should be shared between two Pb atoms, and the other two I atoms should remain unshared to make a total of 4*(1/2) + 2 = 4 I atoms per Pb. There are two possible structures satisfying this—a one dimensional chain of edge-shared PbI₆ octahedra (Fig. 2, **A**) and a two-dimensional sheet of corner-shared PbI₆ octahedra (Fig. 2, **B**). A third possible structure is indeed the molecular crystal made up of tetrahedral PbI₄ molecules (Fig. 2, **C**). We also considered a one-dimensional chain of corner-shared trigonal bipyramids, which however, after relaxation went to the molecular crystal.



Figure 2. Some possible structures for PbI₄. A) Linear chain of edge-shared PbI₆ octahedra (12-Pb-6 hypervalent).
B) Two dimensional sheet of corner-shared octahedra (12-Pb-6 hypervalent). C) Molecular crystal.

What makes PbI₄ unstable? As per literature, PbI_4 is unstable and would decompose to PbI_2 and I_2 .⁶ Thus we have to assume that all the three structures shown in Fig. 2 are unstable. What is common for these three structures? What is uncommon between these structures and the stable PbI_2 and BiI_3 ? To answer this, the bonding nature of all these structures needs to be studied.

The 1-D chain and 2-D sheet structures shown in Fig. 2, A and B are hypervalent systems, and hence we prefer to use the N-X-L nomenclature of hypervalent systems, where N is the number of valence electrons around the central atom, X is the symbol of central atom and L is the coordination number of the central atom.²³ A hexacoordinate hypervalent system can be of 12-X-6 (eg. SF₆) or 14-X-6 type (eg. XeF₆), in the latter, the antibonding combination of valence s orbital of the central atom with the ligand orbitals (which we call σ_1^* from now onwards) is occupied (see the MOs in Fig. 3).¹⁰ 14-X-6 hypervalent systems are common for heavy central atoms, because for them the relativistically contracted s orbitals will have poor overlap with the orbitals of the central atom with the ligand orbitals are occupied, the s orbitals do not contribute anything towards bonding, or can be said that they stay inert. In other words, the tendency of heavy main group atoms to form 14-X-6 hypervalent systems is a manifestation of inert pair effect. Interestingly, the stable iodides, PbI₂ and BiI₃ are 14-X-6 systems, whereas the 1-D chain and 2-D sheet of PbI₄ (Fig. 2, A, B) are 12-X-6 systems, as illustrated below.

In PbI₂, all the I atoms are tricoordinated with trigonal pyramidal geometry and have one lone pair. The remaining 5 electrons on each I are shared by three Pb atoms. Thus each Pb gets a total of (5/3)*6 = 10 electrons from 6 I atoms. This plus the 4 electrons from Pb makes it a 14-Pb-6 hypervalent system. In BiI₃, each I is dicoordinate, implies, they have two lone pairs, and contribute 3 electrons for bonding. These 3 electrons are shared by 2 Bi atoms. Thus each Bi atom gets a total of (3/2)*6 = 9 electrons from 6 I atoms. This plus 5 electrons of Bi makes it a 14-Bi-6 hypervalent. Therefore in both PbI₂ and BiI₃, the σ_1* is occupied.

In the 1D-chain of PbI₄ (Fig.2, A), the dicoordinate I atoms contribute 3 electrons for bonding which is shared by two Pb atoms; each Pb gets 3/2 electrons from one dicoordinate I. Thus the total number of valence electrons around Pb is 12 (4*(3/2) from the dicoordinate I atoms + 2 from the unshared I atoms + 4 from Pb) which makes it a 12-Pb-6 hypervalent system. Similarly, we can find that the 2-D sheet (Fig. 2, B) is also a 12-Pb-6 system. Therefore in both the 1-D chain and 2-D sheet structures of PbI₄, the σ_1 * is unoccupied. It is very much likely that both of these are metallic due to the low-lying σ_1 *.

The molecular crystal (c) is made up of Lewis octet molecules (8-X-4), and the σ_1^* is unoccupied here as well. The σ_1^* orbital of octahedral, trigonal bipyramidal and tetrahedral systems are shown in Fig. 3. The empty σ_1^* orbitals are good acceptors of electrons (when the central atom is heavy), and hence whenever, a donor is available with appropriate energy, it can interact with it. This gives a hint on the possible decomposition pathway of not only PbI₄, but of any inorganic iodide or bromide of heavy main group atoms, where the σ_1^* is unoccupied.



Figure 3. Schematic representation of the LUMO (σ_1^*) of 12-X-6, 10-X-5 and 8-X-4 (Lewis octet) systems. (X is the symbol of central atom; the number preceding X is the number of valence electrons around the central atom; the number after X is the coordination number of X.

As discussed above the structures shown in Fig. 2 A, B and C will have low-lying LUMO (σ_1^*), which can be a good acceptor for electrons. As the bond order decreases and the bond length increases with hypercoordination, the stability of the σ_1^* of 12-X-6, 10-X-5 (trigonal bipyramidal hypervalent system) and 8-X-4 systems might be in the order 12-X-6 >10-X-5 > 8-X-4. The reactivity might follow the same order. For example, PbI₄, SbI₅ and TeI₆ have the LUMO energies in the order PbI₄ > SbI₅ > TeI₆ (order of increasing hypercoordination) and the HOMO-LUMO gaps in the order PbI₄ > SbI₅ > TeI₆ (see Table 1). From Table 1, we can also see that the HOMO-LUMO gaps for PbI₄, PbI₅⁻ and PbI₆²⁻ follows the order PbI₄ > PbI₅⁻ > PbI₆²⁻, consistent with our argument that the LUMO (σ_1^*) stabilizes with increasing hypercoordination. However, one cannot compare the LUMO energies in this case, as the increasing negative charge will raise the energy of all the orbitals. An immediate inference from the above discussion is that the hypervalent structures of PbI₄ (Fig. 2, A and B) will be kinetically less stable than the molecular crystal, as the former two will have very low-lying, unoccupied σ_1^* , making them reactive. On the other hand, in the case of PbI₄²⁻, where the σ_1^* is occupied, the preferred structure is likely to be hypervalent. In agreement with this, PbI₄²⁻ is known experimentally with counter-cations, and the structure is made up of PbI₆ octahedra (similar to Fig. 2 A and B).^{24,25,26,27}.

Table 1. LUMO-energy, HOMO-LUMO gap and average bond lengths of the compounds discussed in this work. The data is based on calculations using M06-2X functional and Def2-TZVPD basis set.

	LUMO-energy (eV)	HOMO-LUMO gap (eV)	Average bond length (Å)
PbI ₄	-4.13	5.03	2.75
PbI ₅ -	-1.03*	3.80	2.88
PbI ₆ ²⁻	1.81*	3.37	2.98
PbBr ₄	-4.07	6.14	2.54
PbCl ₄	-3.91	7.29	2.38
PbF ₄	-4.40	9.76	1.97
PbH ₄	-0.22	9.69	1.75
Pb(CH ₃) ₄	-0.05	8.30	2.23 (Pb-C)

TeI ₆	-5.35	3.21	2.79
SbI ₅	-4.33	4.20	2.74
TeI ₆ ²⁻	3.88*	4.92	2.95
SbI ₅ ²⁻	4.22*	4.88	3.00

* The LUMO energies, or in general the orbital energies will lower further in presence of counter-cations

From the above discussion, we expect that the most stable form of PbI₄ should be a molecular crystal made up of tetrahedral PbI₄ units (which indeed we confirm later in this paper by calculations on extended structures). Let us take TeI₆, SbI₅ and PbI₄ as examples for the 12-X-6, 10-X-5 and 8-X-4 systems. Iodine atoms are not very electronegative. Hence their lone-pair combinations will be sufficiently high in energy to interact with the lowlying σ_1^* of another molecule. This type of reactivity, schematically shown in Fig. 4, would destabilize these compounds. For SbI₅ and PbI₄ and TeBr₆, we calculated the transition states for their bimolecular decomposition (see Fig. 5) which are perfectly in tune with the reactivity represented in Fig 4. All the barriers are low indicating their kinetic instability. As already mentioned, the reactivity order of the LUMOs of TeI₆, SbI₅ and PbI₄ might be in the order TeI₆ > SbI₅ > PbI₄, as the LUMOs gets destabilized and HOMO-LUMO gap increases in the same order. Accordingly, the barrier for SbI₅ decomposition is lower than that for the decomposition of PbI₄. The barrier for TeI₆ decomposition should be smaller than the 7 kcal/mol for SbI₅, and hence can be even barrier-less (no transition state). As a result, we could not locate the transition state for TeI₆ decomposition. However, we could obtain a transition state for TeBr₆ decomposition, which again is in accordance with the reactivity shown in Fig. 4.



Figure 4. Schematic representation of the bimolecular decomposition channel of the 12-X-6, 10-X-5 and 8-X-4 systems, when the central atom is heavy and the ligands carry p-type lone pair.

Though we did not find a transition state for TeI_6 decomposition (barrier-less reaction) we found that a radical dissociation to TeI_5 and I is exergonic at room temperature by 6 kcal/mol, which clearly says that it should be unstable. The I radical so formed can then abstract an I from TeI_5 radical to form TeI_4 and I_2 .



Figure 5. Decomposition mechanisms of SbI₅, PbI₄ and TeBr₆, calculated at M06-2X/Def2-TZVPD level of theory. Red, yellow, blue, deep pink and pale pink colored spheres indicate Pb, Br, I, Sb and Te respectively.

Table 2. Gibbs energy of activation for TeX₆, SbX₅ and PbX₄, where X = I, Br, Cl, calculated at M06-2X/Def2-TZVPD level of theory.

	$\Delta G^{\#}$ (kcal/mol)		$\Delta G^{\#}$ (kcal/mol)		$\Delta G^{\#}$ (kcal/mol)
TeI ₆	(barrier-less)	SbI ₅	7	PbI ₄	22
TeBr ₆	18	SbBr ₅	31	PbBr ₄	42
TeCl ₆	49	SbCl ₅	64	PbCl ₄	63

Table 2 shows the barriers for the decomposition of PbI₄, SbI₅ and TeI₆ and their analogs with lighter halogens. The geometry of the transition state does not change much with changing the halogen, but the barrier does. As is evident from the table, the barrier increases with increasing electronegativity of the halogen. This is because, as the electronegativity of the halogen increases, the lone pair combinations centered on them becomes very low-lying and hence energetically away from the LUMO (as can be seen in the HOMO-LUMO gaps listed in Table 1). This makes the donor-acceptor interaction as shown in Fig. 4 less stabilizing, thus increasing the barrier. Relativistic calculation with ZORA approach as implemented in the program ORCA, gave a barrier of 26 and 44 kcal/mol for the decomposition of PbI₄ and PbBr₄, not much different from the values shown in Table 2.²⁸⁻³² One has to note however that the barrier reported in Table 2 are based on gas phase calculation where the translational entropy decrease as we go from reactant to the transition state is overestimated. Removing the translational entropy contribution, would decrease the barrier by ~ 10 kcal/mol in all the cases. This is important as heavy metal bromides and iodides are less likely to be in gas-phase at ambient conditions, due to the higher inter-molecular dispersion interactions.

An interesting point to be noted here is that the decomposition of PbX_4 results in the formation of PbX_2 , which is reactive due to the presence of an unoccupied orbital, and the reactivity being further enhanced by the lone-pair on X. Thus the PbX_2 formed can react with PbX_4 , with even low barrier, and can cause decomposition of the PbX_4 to PbX_2 and X_2 , as shown in Fig. 6. Thus, once a few molecules of PbX_2 are formed by bimolecular reaction as shown in Fig. 5, they can cause rampant decomposition of the remaining PbX_4 molecules via the low-barrier route shown in Fig. 6. This explains the instability of $PbBr_4$, and PbI_4 .



Figure 6. Low-barrier decomposition of PbX₄ caused by the presence of PbX₂. The activation free energies (ΔG) for X = Cl, Br and I are also shown. The structure labelled # is the transition state.

Why alkyl substituents stabilize the higher oxidation state of heavy atoms? Having explained the instability of compounds such as PbI₄, SbI₅, TeI₆, and TeBr₆ as due to a donor-acceptor interaction where the donor is the lonepair on the substituents, the stability of alkyl (-R) substituted analogs such as PbR₄, SbR₅ or TeR₆ becomes evident. Because there are no lone pairs on alkyl substituents to cause such decompositions. While Pb(CH₃)₄, Sb(CH₃)₅ and Te(CH₃)₆ are minima, we could not locate a decomposition pathway similar to PbI₄. Also notice that dissociation of PbX₄ to PbX₂, does not mean that Pb is dicoordinated in PbX₂. Pb in PbX₂ is actually hypercoordinated, due to the participation of lone pairs on halogen in bonding (see Fig. 1). On the other hand, in PbR₂, this is not possible, and hence the vacant p orbital on Pb has to be coordinated to some Lewis base to make it stable (or one need very bulky substituents to protect kinetically).^{33:34} That is why Pb forms mostly tetravalent compounds with organic substituents.^{35:36}

Is the molecular crystal the most stable form of PbI4 with Pb in +4 oxidation state?

In Figure 2 we have introduced some possible structures of PbI₄, and via a qualitative reasoning proposed that the molecular crystal will be the most stable structure of PbI₄. The Open Quantum Materials Data base reports the Pb-I phase diagram and five compounds corresponding to PbI₄ composition.^{37:38} These structures further relaxed by us are shown in Fig. 7 along with the relative energy values (per formula unit). We can infer that they indeed have got the molecular crystals (**a** and **b**, Figure 7) and the one dimensional chain, **c** and as we predicted, **c** is metallic due to the low-lying σ_1^* orbitals.



Figure 7. Structures of PbI₄ reported in the OQMD and further relaxed by us. Relative energy values (per formula unit) are shown in parentheses. Bader charge on I atoms are shown in red color.

We were surprised by the fact that \mathbf{c} was as stable as the molecular crystals which is in stark contrast to what we anticipated. This made us to check whether \mathbf{c} is really a Pb(IV) system. We performed a Crystal Orbital Hamilton Population (COHP) analysis (Fig. 8, C). It was found that some σ_1^* levels are occupied and some I-I antibonding levels (antibonding combination of lone pairs on I) are emptied. If \mathbf{c} was a Pb(IV) system, the σ_1^* level will be unoccupied, and the lone pairs on I will be intact, meaning both the bonding and antibonding combinations of the lone pairs will be occupied. Thus the COHP analysis implies the transfer of electron density from I lone pairs to σ_1^* . To verify this we visualized the highest occupied and lowest unoccupied crystal orbitals at the Gamma point and found that these are constituted by the antibonding combination of lone pairs on I. The transfer of electron density from the lone pairs on I (mono-coordinate I) to the σ_1^* results in a decreased negative charge on these I atoms as can be seen from the charges shown in Fig. 7. All these results suggest that Pb in \mathbf{c} is partially reduced and hence \mathbf{c} is not a Pb(IV) system.



Figure 8. Lowest unoccupied crystal orbital, LUCO (A) and highest occupied crystal orbital, HOCO (B) of structure **c** at Gamma point. (C) COHP diagram of **c** for the Pb-I and I-I contacts. COHP suggest that both the I-I and the Pb-I weakly antibonding levels are partially filled.

Structure **d** can be considered as a PbI₂-ribbon with empty p orbital on Pb (this is explained at the end of this paragraph) that interact with the lone pair on I of I₂ molecules. Thus **d** is a Pb(II) system. The Bader charge distribution (Fig. 7, charges are shown in red color) showed that the I forming the I-I bonds carry negligible negative charge, indicating that they are oxidized (or Pb is reduced). The description of PbI₂ ribbon in **d** is based on the electron counting scheme we introduced earlier in this work. The I atoms in the PbI₂ ribbon are dicoordinate and hence will donate 3 electrons for bonding, which is shared by two Pb atoms. Thus each Pb gets (3/2)*4 = 6 electrons from I. This plus 4 electrons from Pb makes it a 10-Pb-4 hypervalent system, which has two electron lesser than analogous XeF₄, which has a lone pair on perpendicular p orbital. This is the reason for assuming an empty p orbital on Pb that can interact with lone pairs of I₂.

The most stable structure **e** can be understood as a dimer of $PbI^+I_3^-$, which is justified by the charge distribution. Notice that the end iodine atoms of the I₃ fragment in **e** carry large negative charge, very similar to I₃⁻. Structure **e** is the only thermodynamically stable phase corresponding to PbI_4 composition on the Pb-I phase diagram, and all others are meta-stable, according to the OQMD data. Among the stable and metastable phases, the molecular crystal is the only true Pb(IV) system. The molecular crystal being metastable is prone to decomposition/phase transformation, however if the barrier for decomposition is high, it cannot.

The two-dimensional sheet structure is not present in the OQMD. Hence we calculated this structure both at large and small inter-chain separation (Fig. 9). At large separation, the sheet is a Pb(IV) system (**f**) and is much less stable than the molecular crystal, which is in well accordance what we explained earlier in this work. This is metallic, due to the presence of low-lying σ_1^* . This is supported by COHP diagram (Fig. 9) which shows that the levels around the Fermi level are Pb-I antibonding (weakly antibonding, due to the poor overlap of 6s of Pb). Allowing the sheets to interact resulted in I-I bond formation and hence reduction of Pb (**g**). Structure **g** can be understood as a PbI₂ sheet with empty perpendicular p orbital interacting with lone pairs on I of I₂ molecule. The Bader charge on the I atoms involved in I-I bonding are only slightly negative (-0.05 and -0.07), clearly suggesting that they are oxidized. The COHP diagram (Fig. 9) indicates that the levels which are weakly antibonding between

Pb and I (σ_1^*) are fully occupied (compare with **f**), and some I-I antibonding levels are emptied. This indicates oxidation of I and reduction of Pb. Thus **g** is not a Pb(IV) system.



Figure 9. Two-dimensional sheet structure of PbI_4 calculated at large inter-layer separation, **f**. Allowing the layers to interact gave structure **g**. Energy (per formula unit) relative to **c** is shown in parentheses. The COHP diagrams corresponding to **f** and **g** are shown below the respective structures.

From the above analysis, it is evident that the molecular crystal is the most stable form of PbI₄ with Pb in +4 oxidation state. We wanted to check whether the mechanism we described in the gas phase calculations is valid here as well. The mechanism of PbI₄ decomposition shown in Fig. 5 involves a donor acceptor interaction between the σ_1^* of one PbI₄ and lone pair on I of another PbI₄ and vice versa. From orbital interactions, we were aware that a distortion to a C_{2v} structure by opening up of a bond angle can stabilize σ_1^* of tetrahedral molecule (see SI). Therefore we imagined that the solid state decomposition of PbI₄ might involve a transition state with opened up bond angle. Our reactant is **c**. To get the product geometry, we increased one bond angle and relaxed by keeping the cell fixed. Interestingly, it relaxed to structure **h**, which can be understood as an ionic crystal made up of PbI⁺ and I₃⁻ similar to **e**. Nudged elastic band calculation was performed to calculate the activation energy and the reaction path that connect **c** and **h** (Fig. 10). The activation energy for the conversion of **c** to **h** is only 1.3 kcal/mol, clearly indicating kinetic instability of **c**. It is interesting to note that **h** is analogous to the well-known TII₃ structure. Thus the molecular crystal is not only a metastable phase but also kinetically unstable with respect the phase transformation to a Pb(II) structure (**h**).

In overall, we have found here that the molecular crystal (metastable phase) which is the only Pb(IV) system in the Pb-I phase diagram is kinetically unstable both by molecular and solid state calculations—both decomposition pathways caused by low-lying σ_1^* and the lone-pairs on I. This is an escape route not only for PbI₄,

but for any heavy metal iodide, where the σ_1^* orbital is unoccupied which usually happens when the metal is its higher oxidation state. Thus our study explains the instability of iodides (and also of bromides) of heavy metal atoms in their higher oxidation state.



Figure 10. Decomposition of $PbI_4(\mathbf{c})$ to $PbI^+I_3^-(\mathbf{h})$. The transition state geometry is obtained from NEB calculation. The activation energy is only 1.3 kcal/mol and the reaction is exo-energetic by 9 kcal/mol.

Computational Details: The calculations reported here are done with M06-2X functional and Def2-TZVPD basis set using G16 program.^{39,40} Grimme's D3 dispersion correction is accounted for all the reported results.^{41,42} Wave function stability was ensured in all cases. Superfine grid was used in all the geometry optimizations. Intrinsic Reaction Coordinate calculation was done on the located transition states to confirm that they connect the proper reactant and product. The reaction barriers reported are the Gibbs energy of activation, at temperature 298.15 K. Further validation of the results were done here with relativistic Zeroth Order Regular Approximation (ZORA) as implemented in the ORCA program. Segmented all electron relativistically contracted (SARC)-ZORA-TZVP basis set was used for Pb and ZORA-TZVP was used for other atoms.²⁸⁻³²Plane-wave calculations were done using Quantum Espresso program, with Projector Augmented Wave pseudo potential and PBE functional.^{43,44,45} Kinetic energy cut-off was selected according to the minimum cut-off mentioned in the pseudo potential file. Charge density cut-off was set to four times the kinetic energy cut-off. For comparison of energy of different polymorphs, k-spacing of 0.2 Å⁻¹ is used. The quantum espresso input generator tool of "materials cloud" was used to generate k points corresponding to this spacing.⁴⁶ The pseudo potentials employed were downloaded from Materials cloud.⁴⁷ The convergence thresholds for SCF, energy and force were 1.0E-06, 1.0E-04 and 1.0E-03 respectively. Variable-cell relaxation was used for structure optimization in all the cases, with no space group symmetry imposed—i.e. "ibrav" was set to zero. Bader charge analysis was done by using the code provided by the Henkelman group.⁴⁸

CONCLUSIONS

Relativistic contraction of s orbitals of heavy atoms, has profound effects on the stability of compounds - *depending* on the nature of substituents. The contracted valence s orbital of heavy atoms will have poor overlap with the orbitals of the substituents, and results in poor splitting of bonding and antibonding levels. The low-lying antibonding orbital (σ_1 *) so formed, essentially makes such systems strong acceptors of electrons and hence reactive. When the substituents are less electronegative, and carries lone pairs (such as iodine), the lone-pair combinations will be closer in energy to the σ_1 *. A donor-acceptor interaction between these would decompose

such structures, and results in the reduction of the central metal atom. This explains the instability of compounds such as PbI₄, SbI₅, TeI₆, BiI₅, TeBr₆ etc. or in general, any heavy metal iodide or bromide, where σ_1^* is vacant. When two electrons are added to these compounds, to form their dianions, they become stable, as the low-lying σ_1^* becomes occupied, and hence the aforementioned reactivity is hindered. Compounds such as PbR₄, SbR₅, TeR₆ etc., where R is alkyl group are stable with respect to the decomposition, due to the unavailability of lone pairs on the substituents. The instability of iodides of heavy atoms, where the σ_1^* is unoccupied, is common to both molecular and extended structures. Our study opens up a way to approach the instability issues of inorganic compounds from a molecular perspective.

ASSOCIATED CONTENT

Supporting Information. Coordinates and energies of all the calculated structures, NEB reaction path, input files for solid state calculations, schematic showing stabilization of LUMO of PbI₄ by second order interaction.

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Notes

Authors declare no competing financial interests.

ACKNOWLEDGMENT

PCP thanks DST India for providing research grant through Inspire Faculty Fellowship.

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TOC Graphic



Stable, when the central atom is very heavy. Good acceptor.



High-lying, when the ligands are less electronegative. Good donor.



Intermolecular donor-acceptor interaction, causing decomposition.