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Metastable behavior of Noble Gas inserted Tin and Lead Fluorides

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Abstract

Ab initio computations are carried out to explore the structure and stability of $FNgEF_3$ and FNgEF (E = Sn, Pb; Ng = Kr-Rn) compounds. They are the first reported systems to possess Ng-Sn and Ng-Pb bonds. Except $FKrEF_3$, the dissociations of $FNgSnF_3$ and FNgEF producing Ng and SnF_4 or EF_2 are only exergonic in nature at room temperature whereas $FNgPbF_3$ has thermochemical instability with respect to two two-body dissociation channels. However, they are kinetically stable having positive activation barriers (ranging from 2.2 to 49.9 kcal/mol) with respect to those dissociations. The kinetic stability gradually improves in moving from Kr to Rn analogues. The remaining possible dissociation channels for these compounds are found to be endergonic in nature. The nature of bonding is analyzed by natural bond order, electron density, and energy decomposition analyses. Particularly, natural population analysis reveals that they are best represented as $F^-(NgEF_3)^+$ and $F^-(NgEF)^+$. All the Xe/Rn-E bonds in $FNgEF_3$ and FNgEF are covalent in nature.

Keywords: *Ab initio* study, dissociation channels, kinetic stability, natural population analysis, electron density analysis, energy decomposition analysis

Introduction

For a long time, chemists had been facing a challenge to make noble gas (Ng) as a bonding partner due to their very unreactive nature. Earlier attempts to synthesize[1] noble gas compounds on the basis of theoretical predictions[2] were not convincing. Later, Pauling on the basis of ionic radii of different Ng atoms predicted the existence of Ag_4XeO_6, AgH_3XeO_6, KrF_6 and XeF_6.[3] Experimental efforts towards the achievement of these predictions were found to be challenging,[4] and it was only in 1962 when Bartlett[5] and others[6-8] announced the preparation of first noble gas compounds. Since then several researchers have either experimentally detected[9-13] or theoretically predicted a large number of Ng compounds.[14-20] As a result, more than 500 such compounds have already been detected,[21] and literature contains excellent review articles[22-25] on this subject as well. Interest in Ng-C compounds grew with the reporting of first Xe-C bond in $XeCH_3^+$ by Holtz and Beauchamp[26] in 1971 followed by the reporting of $Xe(CF_3)_2$ in 1979 and pentafluorophenylxenon cation in 1989.[27] Subsequently there has been a plethora of work reported in the field of Xe-C containing organoxenon derivatives.[28] Under cryogenic environment, different Xe-C containing compounds such as HXeCN,[9d] ClXeCN,[29a] BrXeCN,[29a] HXeCCH,[29b] HXeCCXeH,[10d] HXeCCF,[29c] $HXeC_3N$[29d] and $HXeC_4H$[9j] were reported. Theoretical studies have also immensely contributed to the discovery of different xenon-carbon compounds.[30] Efforts towards syntheses of compounds with Xe-Si and Xe-Ge bonds are currently being explored. The gaseous trifluorosilylxenon, $F_3Si\text{-}Xe^+$ was detected by spectroscopic techniques, and, also examined by computations.[31,32] We have recently assessed the stability of $NgSiX_3^+$ (X = H, F-Br) clusters.[15h] The inserted Xe compound on SiF_2 resulting in the formulation of FXeSiF[33] was also reported. Recently, the gaseous trifluorogermylxenon cation, $F_3Ge\text{-}Xe^+$ was observed by means of mass spectroscopic techniques.[34] Grandinetti and co-workers[35] explored the stability of neutral $FXeGeF_n$ (n = 1, 3) compounds with xenon-germanium bonds. They showed that such molecules are thermochemically stable with respect to all possible dissociation channels except the dissociation into Xe + GeF_{n+1}; however, they are kinetically stable with respect to that dissociation. Yockel et al.[36] theoretically predicted the stability of $FKrGeF_3$, the only known neutral compound with Kr-Ge bond. Chemistry related to the

Ng-compounds having bonds between Ng and heavier congeners than Ge is still unexplored.

The present study is an effort to bridge that gap. Here, we have presented for the first time the neutral compounds, $FNgEF_3$ and FNgEF (Ng = Kr, Xe, Rn; E = Sn, Pb) having Ng-Sn and Ng-Pb bonds. Their thermochemical and kinetic stabilities are assessed by computing the dissociation energy, enthalpy change, free energy change and activation barrier of different probable dissociation channels. $FNgSnF_3$ (Ng = Xe, Rn) and FNgEF (Ng = Kr, Xe, Rn) are found to be thermochemically stable with respect to all probable dissociation channels except a two-body dissociation channel producing Ng and EF_4 or EF_2. $FNgPbF_3$ compounds are found to be thermochemically unstable with respect to two two-body dissociation channels. However, they are kinetically protected with respect to these dissociations. The bonding situation is analyzed by natural bond order, electron density and energy decomposition analyses.

Computational Details

The geometry optimizations for all the studied systems are performed at the MP2[37]/def2-TZVPPD[38] level by using the Gaussian 09 program package.[39] A quasi-relativistic pseudopotential is used for core electrons of Sn, Pb, Xe, and Rn atoms.[40] The characterization of the stationary state as of minimum energy or transition state (TS) is done by computing harmonic vibrational frequencies. We have also computed intrinsic reaction coordinates (IRC) to ensure that the transition states are connected with the desired minima along the minimum energy path (see Figure S1 in the supporting information). Taking the FNgEF set (E = Sn, Pb), optimizations and frequency calculations are also carried out at the CCSD(T)[41]/def2-TZVP[39] level to ensure that these minima are not an artifact of the MP2 level. The structural parameters obtained from the CCSD(T)/def2-TZVP computations are provided in Table S1 (supporting information) and here we continue with the results obtained at the MP2/def2-TZVPPD level. The natural bond order (NBO) analysis is performed as implemented within Gaussian 09 program.[39] The atoms-in-molecules (AIM)[42] analysis is carried out by using Multiwfn software[43] at the MP2/def2-TZVPPD/WTBS[44] level taking the optimized geometries at the MP2/def2-TZVPPD level. All electron WTBS[44] basis set is used for Sn, Pb, Xe, and

Rn. The electron density ($\rho(r_c)$), the Laplacian of the electron density ($\nabla^2\rho(r_c)$), the total electron energy density ($H(r_c)$), the local kinetic energy density ($G(r_c)$) and the local potential energy density ($V(r_c)$) at the bond critical points (BCPs) are also computed. We have further considered the classifications as was done by Boggs and co-workers.[45] They classified the covalent bonds into four types:

Type A. $\nabla^2\rho(r_c) < 0$, and $\rho(r_c)$ is large (≥0.1 au)

Type B. $H(r_c) < 0$, and $\rho(r_c)$ is large (≥0.1 au)

Type C. $H(r_c) < 0$, and $G(r_c)/\rho(r_c) < 1$

Type D. $|H(r_c)|$ is small (< 0.005 au) and $G(r_c)/\rho(r_c) < 1$

The same authors[45] also proposed two new categories viz., W^c (weak interaction having some degree of covalent character) and W^n (weak interaction having noncovalent character) depending on the bond lengths.

The energy decomposition analysis[46] (EDA) is carried out at the revPBE-D3[47]/TZ2P[48]//MP2/def2-TZVPPD level using ADF(2013.01) program package.[49] Scalar relativistic effects are included for the heavier atoms using the zeroth-order regular approximation (ZORA).[50]

Structure and stability

The structures of the minimum energy states and transition states of $FNgEF_3$ and FNgEF (E = Sn, Pb; Ng = Kr-Rn) compounds are pictorially depicted in Fig. 1. All the $FNgEF_3$ compounds correspond to C_{3v} point group with $^1A_1$ electronic state. However, their geometries change to have a C_s point group while they pass through transition state structure corresponding to the dissociation of $FNgEF_3$ into Ng and EF_4 (**TS-1** in Fig. 1). On the other hand, all FNgEF compounds have planar geometries with C_s point group and ^{1}A' electronic states which adopt non-planar geometries having C_1 point group in the transition states associated with the dissociation of FNgEF into Ng and EF_2 (**TS-2** in Fig. 1). The transition states obtained for the dissociation of $FNgPbF_3$ into NgF_2 and PbF_2 also correspond to C_1 point group (**TS-3** in Fig. 1). The possibility of the existence of higher spin states is also verified but they are found to be higher energy structures.

The different geometrical parameters of these $FNgEF_3$ and FNgEF compounds along with their transition state structures are provided in Tables S2 and S3 (Supporting

Information). The F-Ng-E moieties in $FNgEF_3$ compounds are linear. The Ng-E-F angle gradually increases from Kr to Rn. It shows that the bending of F-E-F moieties in EF_3 away from the bound Ng direction becomes gradually larger in heavier Ng bound analogues, being the largest in Rn case. In the energy minimum structures of FNgEF compounds, the F-Ng, Ng-E and Sn-F bond distances are somewhat larger than those in $FNgEF_3$ revealing their less compactness. Unlike $FNgEF_3$, the F-Ng-E moieties in FNgEF are not perfectly linear, rather somewhat (*ca*. 0.1°-3.6°) bent from the absolutely linear arrangement. In **TS-1** and **TS-2**, the F atom is bonded to Ng in a tilted fashion with the mode of imaginary frequency as the bending of F-Ng-Sn having F-Ng-E angle of 95.0°-130.6°. In **TS-3**, one F atom in PbF_3 is found to be in a bridging position in between Pb and Ng. The mode of the imaginary frequency is associated with the shifting of this bridging F center towards Ng atom and other F atom attached with Ng atom moves in such a fashion that it gives NgF_2 a linear structure. The Pb-F (bridged) bond length is larger by about 0.1 Å than the other two Pb-F bonds. The Pb-Ng bonds are also found to be larger by 0.19 Å in Xe and 0.16 Å in Rn analogues than those in the corresponding minimum energy structures (see Table S3 in supporting information).

Other detailed geometrical changes in moving from minimum energy structures to the respective transition states or from Kr compounds to their heavier analogues are provided in the supporting information. It may be noted that the Ng-E bond lengths in FNgEF are somewhat larger than those in $FNgEF_3$. The shorter Ng-E distances in $FNgEF_3$ may be related to the fact that the Ng atoms in $FNgEF_3$ bear larger positive charge (ranging +0.49 to +0.94 e^-) than those in FNgEF (ranging +0.20 to +0.44 e^-). Ng atoms generally do not take part in chemical bonding due to their fulfilled valence shell configuration. Therefore, the Ng atoms having larger positive charge would be more effective candidates in forming chemical bond than that having less positive charge. An anomalous result is found in FKrPbF, where the Kr-Pb bond length is about 0.04 Å shorter than that in $FKrPbF_3$.

The IR frequencies along with the IR intensities for different vibrational modes of $FNgEF_3$ and FNgEF compounds are tabulated in Tables S4 and S5 and discussed in the supporting information.

In order to understand the stability of presently investigated compounds, ZPE corrected dissociation energy (D_0), dissociation enthalpy (ΔH) and free energy change (ΔG) for different dissociation channels of $FNgEF_3$ and FNgEF compounds computed at the MP2/def2-TZVPPD level are displayed in Tables 1 and 2. Here, ΔH and ΔG values are calculated at 298.15 K. The dissociation pathways are illustrated by Eqs. 1 - 4 (here, n = 1, 3):

$$FNgEF_n \rightarrow F + Ng + EF_n \quad (1)$$

$$FNgEF_n \rightarrow NgF_2 + EF_{(n-1)} \quad (2)$$

$$FNgEF_n \rightarrow F^- + NgEF_n^+ \quad (3)$$

$$FNgEF_n \rightarrow Ng + EF_{(n+1)} \quad (4)$$

The three-body (3-B) dissociations for all $FNgEF_3$ and FNgEF compounds are shown to be endothermic; however, the dissociation processes of FNgEF are more endothermic than those of $FNgEF_3$. For $FKrPbF_3$, the D_0 value is negative (-0.2 kcal/mol) and 3-B dissociation is only slightly endothermic in nature (ΔH = 0.3 kcal/mol). In case of $FKrSnF_3$, the dissociation energy (D_0 = 7.6 kcal/mol) and endothermicity (ΔH = 8.2 kcal/mol) are also quite low. In such dissociation process, since entropy change (ΔS is positive) is a favorable term, we have also computed free energy change (ΔG). The 3-B dissociations of $FKrEF_3$ compounds are spontaneous at room temperature as indicated by negative values (-7.8 and -14.8 kcal/mol for $FKrSnF_3$ and $FKrPbF_3$, respectively) of ΔG. Except $FKrEF_3$, in all other cases the unfavorable ΔH values for these 3-B dissociations are so large that favorable ΔS term cannot overshadow them. In both $FNgEF_3$ and FNgEF cases, the stability with respect to the 3-B dissociation gradually improves along Kr to Rn. This corroborates well with the WBI values of Ng-Sn bonds, which depict more covalent character in moving from Kr to Rn (*vide infra*). Note that despite higher WBIs and compactness in $FNgEF_3$ than those in FNgEF, the corresponding D_0 values for the 3-B channels are smaller in the former case than that in the latter. The difference in the stability of dissociated EF_3 and EF products and the charge on the respective atoms of the bound systems are presumably the reasons behind this.

The two-body (2-B) dissociations (Eq. 2) of $FNgSnF_3$ and FNgSnF producing NgF_2 and SnF_2 or Sn are also endergonic in nature, which are more unfavorable in latter

cases than those in the former. However, unlike Ng-Sn complexes, this 2-B dissociation of $FNgPbF_3$ generating NgF_2 and PbF_2 are exergonic in nature at room temperature. The activation barriers ($\Delta E^{\ddagger}$) for this dissociation are found to be 13.8 kcal/mol for Xe and 10.1 kcal/mol for Rn complexes. On the other hand, the dissociations of FNgPbF resulting in NgF_2 and Pb are highly endergonic in nature.

The D_0 values corresponding to the ionic dissociations following Eq. 3 are significantly higher in comparison to that in Eq. 2 in $FNgSnF_3$ whereas the same is smaller in FNgEF cases. Note that the ionic dissociations for $FNgEF_3$ are more endergonic in nature than those in FNgEF. The 2-B dissociations of $FNgEF_3$ and FNgEF as Ng and $EF_{(n+1)}$ (Eq. 4) are highly exergonic in nature. The dissociations of $FKrSnF_3$ and FKrSnF producing Kr and SnF_4 or SnF_2 are almost equally exergonic whereas for Xe and Rn analogues of $FNgSnF_3$ and $FNgPbF_3$ compounds, this 2-B dissociation is slightly less spontaneous in nature than those in FNgEF. However, the $\Delta E^{\ddagger}$ values computed for these dissociation processes are positive, being reasonably high for $FNgFF_3$ but quite low for FNgEF. The $\Delta E^{\ddagger}$ values are 23.9, 32.7 and 36.8 kcal/mol for Kr, Xe and Rn analogues of $FNgSnF_3$, respectively, whereas, the same are 2.9, 6.9 and 8.7 kcal/mol for Kr, Xe and Rn analogues of FNgSnF, respectively. On the other hand, for $FNgPbF_3$ the $\Delta E^{\ddagger}$ values are quite larger than those in $FNgSnF_3$ being 40.5 for Kr, 46.6 for Xe and 49.9 kcal/mol for Rn analogues whereas for FNgPbF, the $\Delta E^{\ddagger}$ values are slightly smaller than those in FNgSnF being 2.2 for Kr, 6.0 for Xe and 7.8 kcal/mol for Rn analogues. Therefore, for a particular type of compounds, the barrier gradually increases in moving from Kr to Rn analogues.

In all cases here, $\Delta E^{\ddagger}$ values are found to be larger with the increased WBI values of Ng-E bonds. Now, let us compare the barrier in the present cases with those found by Hu and co-workers[51] in XNgY type of systems. They argued that 2-B dissociation channel for a system as per Eqs. 2 and 4 must have a minimum barrier of 6, 13 and 21 kcal/mol to have a half-life of 100 s in the gas phase at 100, 200 and 300 K, respectively. Therefore, all $FNgSnF_3$ compounds should be metastable at 300 K or even at higher temperature whereas FXeEF and FRnEF might be detectable at least at 100 K. Due to very low barrier, FKrEF is very unlikely to be detected. Although the barrier for the dissociations of $FNgPbF_3$ following Eq. 4 is large enough to exist at 300K or even at

higher temperature but the barrier corresponding to the dissociation producing NgF_2 and PbF_2 (Eq. 2) implies that $FXePbF_3$ could be metastable up to 200 K whereas for $FRnPbF_3$ lower temperature is needed. The instability of $FKrEF_3$ towards the 3-B dissociation channel also rules out the possibility of its detection.

Nature of bonding

To get an idea about the bonding situation we have computed atomic charges derived from the natural population analysis (NPA) and Wiberg bond indices (WBIs) for each bond of $FNgEF_3$ and FNgEF compounds (see Table 3). According to NPA charge, in both $FNgEF_3$ and FNgEF all F atoms bear negative charges and Ng and E possess positive charges. Ng bears less positive charge in comparison to E atom in all cases. Positive charge on Ng increases on moving from Kr to Rn systems, whereas the positive charge on E decreases along the same. F atom attached to Ng contains more negative charge in comparison to the fluorine atom attached to E except in the cases of $FKrPbF_3$ and $FXePbF_3$, in which the reverse is true. Further, the charge on F bonded to Ng atom is less negative for $FNgEF_3$ systems (range -0.69 to -0.83 e^-) than that in FNgEF systems (range -0.92 to -0.94 e^-). The positive charges on Ng and E centers are comparatively less in FNgEF compounds than those in $FNgEF_3$. Following the charge distribution, these systems could be best represented as $F^-(NgEF_3)^+$ and $F^-(NgEF)^+$. Consequently, the F-Ng bond is essentially an ionic bond. The very low WBI values for F-Ng bonds also describe their ionic character. The F-Ng bonds in FNgEF are even more ionic in nature as indicated by lower WBIs and higher negative charge on F than those in $FNgEF_3$.

In contrast, the Ng-E bonds appear to be covalent in nature. In $FNgEF_3$, the WBIs of Ng-E bonds are within the range of 0.60 to 0.82 whereas those in FNgEF are somewhat smaller than the former cases ranging within 0.38-0.70. Therefore, the degree of covalent character in Ng-E bonds gradually increases in moving from Kr to Rn analogues as indicated by the increased WBI values along the same. Note that lower WBIs for Ng-E bonds in FNgEF than $FNgEF_3$ corroborate well with the fact that the Ng-E bond distances in the latter are shorter than those in the former.

Now, electron density analysis[42] is performed to get more insight into the nature of bonding. Table 4 presents different topological descriptors at the BCPs of F-Ng and

Ng-E bonds of $FNgEF_3$ and FNgEF compounds along with the typical covalent bond distance computed for F-Ng and Ng-E bonds following the studies of Cordero et al.[52] and Pyykkö.[53] In general, negative (electron density concentration) and positive (electron density depletion) values of $\nabla^2\rho(r_c)$ at the BCPs are indicators of covalent and noncovalent bonding, respectively. However, in many cases including the systems containing 3d and heavier atoms it fails to explain a covalent bond (for examples see ref. 54 and pp. 312-314 of ref. 42).

Some other criteria to interpret a covalent bond are also reported in the literature. Such as, if $\nabla^2\rho(r_c) > 0$ and $H(r_c) < 0$ or $G(r_c)/\rho(r_c) < 1$, then the bond might be regarded as a partial covalent bond.[55,56] Moreover, in order to interpret the nature of bonding, we have also included the classifications suggested by Boggs et al.[45] as described in computational details section. Since in all cases $\nabla^2\rho(r_c)$ is positive, therefore it rules out the possibility of type A. The contour plots of $\nabla^2\rho(r_c)$ for $FNgEF_3$ and FNgEF are provided in Figs. 2 and S2 (in supporting information), respectively. No charge concentration is found in between two atoms. Only the shapes of valence orbitals get slightly deformed. Note that $H(r_c)$ values at the BCPs of both F-Ng and Ng-E bonds are negative, even it is more negative in F-Ng bonds than those in Ng-E bonds except FKrEF compounds. On the other hand, $G(r_c)/\rho(r_c)$ values are very small (<0.8) in Ng-E bonds whereas it exceeds the limiting value of 1 in the cases of F-Ng bonds except for the F-Ng bonds in $FKrEF_3$. Therefore, if we follow Boggs' classification,[45] we need to categorize the F-Ng bonds in $FKrEF_3$ as of types B and C both whereas the rest of the F-Ng bonds as of W^c type. However, we have already seen that it would be the best to consider these F-Ng bonds as of ionic type (*vide supra*). It indicates that such classification does not always lead to proper conclusion. All Ng-E bonds fall in the category of C with the criteria of $H(r_c) < 0$, and $G(r_c)/\rho(r_c) < 1$.

It may be noted that in $FNgSnF_3$, the Kr-Sn equilibrium bond distance (r_e) is only 0.07[52]/0.05[53] Å larger than that of corresponding covalent bond distance (r_{cov}) whereas for Xe-Sn and Rn-Sn, r_e values fall perfectly in the range of their reported r_{cov} distances. Therefore, considering their high WBI values, we may treat them as covalent bonds. In FNgSnF compounds, r_e values of Ng-Sn bonds are 0.13[52]/0.11[53] Å for Kr, 0.06[52]/0.14[53] Å for Xe and 0.04[52]/0.11[53] Å for Rn larger than the corresponding r_{cov} values. Therefore,

here also from their WBI values, Xe/Rn-Sn bonds might be called as covalent bonds whereas Kr-Sn might be the border line case between the partial and perfect covalent bonds. In $FNgPbF_3$, the Xe-Pb and Rn-Pb bond distances are almost equal to their r_{cov} distances whereas in FNgPbF compounds, r_e values of Ng-Pb bonds are 0.18[52]/0.19[53] Å for Kr, 0.06[52]/0.17[53] Å for Xe and 0.03[52]/0.13[53] Å for Rn larger than the corresponding r_{cov} values. Therefore, Xe-Pb and Rn-Pb bonds could also be called as covalent bonds.

It may also be noted that the descriptor, $G(r_c)/\rho(r_c)$ represents the bonding situation in the present systems most appropriately. It is around 1 for F-Ng bonds and it is much smaller than 1 for Ng-E bonds. It even gradually decreases for Ng-E bonds along Kr to Rn showing larger covalent character along the same. Further, this value for Ng-E bond is somewhat smaller in $FNgEF_3$ than those in FNgEF implying larger covalency in the former than that in the latter. Therefore, it perfectly tallies with the WBI results. $\nabla^2\rho(r_c)$ does not seem to describe these systems properly.

EDA[46] is also performed to get an idea about the contribution from Pauli repulsion (ΔE_{pauli}), electrostatic (E_{elstat}), orbital (ΔE_{orb}) and dispersion (ΔE_{disp}) energy terms towards the total interaction energy (ΔE_{int}) (see Tables 5 and 6). We have followed the NPA charges obtained on each center to impose the overall charge on a fragment. Since both $FNgEF_3$ and FNgEF could be best represented as $F^-(NgEF_3)^+$ and $F^-(NgEF)^+$, to explore the nature of bonding in F-Ng bonds we have partitioned $FNgEF_3$ and FNgEF into F^- and $[NgEF_3]^+$ or $[NgEF]^+$. In $FNgEF_3$ compounds, since the total charges on fragments [FNg] and [EF_3] are well below $|0.5|\ e^-$, we have considered them as neutral (radical). However, in FNgEF compounds except FRnSnF, the charges on [FNg] and [EF] fragments are larger than $|0.5|\ e^-$. Therefore, for these cases we have performed EDA by considering both radical and charged fragments. The preparation energies of these fragments, interaction energies and dissociation energies computed at the MP2/def2-TZVPPD level are provided in Tables S6 and S7 (supporting information). As expected from the ionic character, in F-Ng bonds the contribution from ΔE_{elstat} is dominant ranging from 60 to 70% towards the total attraction. It may be noted that the contribution from ΔE_{orb} is also quite large (*ca*. 30-40%) in F-Ng bonds. ΔE_{disp} term is not at all important since it contributes the least. In the cases of Ng-E bonds in $FNgEF_3$, ΔE_{orb} is the largest contributor (*ca*. 72-82%) towards the total attraction. Such large

contribution from ΔE_{orb} indicates the nature of Ng-E bonds in $FNgEF_3$ as of covalent type. For these Ng-E bonds, ΔE_{elstat} contributes around 17-27% towards the total attraction. In Ng-E bonds of FNgEF, use of charged fragments leads to ΔE_{elstat} (*ca*. 61-65%) term dominant over ΔE_{orb} (*ca*. 35-38%) whereas the partition into radical fragments yields ΔE_{orb} as the major contributing term (*ca*. 75-79%) towards the total attraction. Therefore, the choice of nature of fragments alters the dominating term in the bonding. It may be noted that in FXeSnF and FRnSnF, the charges on each individual fragment are $|0.55|\ e^-$ and $|0.48|\ e^-$, respectively, whereas in FXePbF and FRnPbF, the charges on each fragment are $|0.59|\ e^-$ and $|0.52|\ e^-$, respectively. Therefore, neither of these two partitioning schemes would represent the actual situation.

Comparison with $FXeGeF_3$ and FXeGeF

To compare our present $FXeEF_3$ and FXeEF cases with $FXeGeF_3$ and FXeGeF reported by Grandinetti et al.[35], we have reoptimized the structures at the same MP2/def2-TZVPPD level. The different geometrical parameters along with a comparative discussion are provided in the supporting information (see Table S8). Here, we have only discussed about their thermochemical and kinetic stabilities and nature of bonding.

The ZPE corrected dissociation energy, dissociation enthalpy and free energy changes for different dissociation channels of $FXeGeF_3$ and FXeGeF are given in Table S9 (supporting information). It may be noted that the 3-B (Eq. 1) and 2-B dissociation channels (Eq. 2) are more endothermic and thermochemically unfavorable for $FXeGeF_3$ compounds than those of Sn and Pb-analogues whereas the ionic 2-B dissociation channels (Eq. 3) are almost equally unfavorable with Sn-analogue. The dissociation of $FXeGeF_3$ into Xe and GeF_4 is more feasible by 14.5 and 42.3 kcal/mol than those of $FXeSnF_3$ and $FXePbF_3$, respectively. The corresponding barrier for the dissociation process of $FXeGeF_3$ is 1.5 kcal/mol smaller than that in $FXeSnF_3$ whereas it is 15.4 kcal/mol smaller than that in $FXePbF_3$. In FXeGeF, the 3-B dissociation is only slightly less unfavorable and other two 2-B dissociations (Eqs. 2 and 3) are more unfavorable than those in FXeSnF and FXePbF. On the other hand, although the dissociation of FXeGeF producing Xe and GeF_2 is more spontaneous than those of FXeSnF and

FXePbF, the barrier is 1.8 and 2.7 kcal/mol larger in the former than those in the latter cases, respectively. Therefore, FXeGeF is more kinetically protected with respect to this dissociation channel than FXeSnF and FXePbF.

NPA reveals that the F-Xe bond in $FXeGeF_3$ is more polarized than those in $FXeSnF_3$ and $FXePbF_3$ but the same in FXeGeF is less polarized compared to FXeSnF and FXePbF (see Table S10 in supporting information). In $FNgEF_3$, the positive charge on Ge center is slightly less than that on Sn center but larger than that on Pb center. The WBI value of Xe-Ge bond in $FXeGeF_3$ (0.720) is only slightly smaller than those in $FXeSnF_3$ and $FXePbF_3$ whereas in FXeGeF the WBI value of Xe-Ge bond is larger than those in the other two compounds.

Different electron density descriptors at the BCPs of F-Xe and Xe-Ge bonds show that they can be categorized as types W^c and C, respectively, similar to those of Xe-Sn and Xe-Pb compounds (see Table S11 in supporting information). However, unlike Xe-Sn and Xe-Pb compounds, $\nabla^2\rho(r_c)$ is negative for Xe-Ge bonds representing the nature of these bonds perfectly. The values of $H(r_c)$ and $G(r_c)/\rho(r_c)$ in both cases are quite comparable, $H(r_c)$ being slightly more negative and $G(r_c)/\rho(r_c)$ being slightly less positive in Xe-Ge bonds than those in Xe-Sn and Xe-Pb bonds.

Conclusion

$FNgEF_3$ and FNgEF (E = Sn, Pb; Ng=Kr, Xe, Rn) compounds might be considered to be the first reported cases of systems having Ng-Sn and Ng-Pb bonds. $FKrEF_3$ compounds are not viable since they are predicted to dissociate spontaneously along a 3-B dissociation channel producing F, Kr and EF_3. The other Ng-Sn compounds are thermochemically stable with respect to all possible dissociation channels except a 2-B dissociation channel, which results in the formation of Ng and SnF_4 or SnF_2. However, they are kinetically stable with respect to this dissociation channel. The activation barrier is larger in $FNgSnF_3$ (23.9-36.8 kcal/mol) than that in FNgSnF (2.9-8.7 kcal/mol) showing higher kinetic stability in the former cases than the latter. The dissociation of $FNgPbF_3$ (Ng = Xe, Rn) compounds is found to be exergonic along two 2-B dissociation channels. The activation barrier for the dissociation of $FNgPbF_3$ into NgF_2 and PbF_2 is 13.8 kcal/mol for Xe and 10.1 kcal/mol for Rn whereas the same for the dissociation into

Ng and PbF_4 is 46.6 kcal/mol for Xe and 49.9 kcal/mol for Rn. On the other hand, FNgPbF compounds are found to be thermochemically stable with respect to all possible dissociation channels except the dissociation into Ng and PbF_2. The corresponding activation barrier is quite low ranging within 2.2-7.8 kcal/mol. For a particular series, the kinetic stability gradually increases along Kr to Rn analogues. Following an argument of Hu et al.,[51] all $FNgSnF_3$ compounds are predicted to be stable at 300 K or even higher whereas $FRnPbF_3$, FXeEF and FRnEF might be metastable at around 100 K. $FXePbF_3$ might be detected at 200 K. The very low barrier suggests the instability of FKrEF to be in such bound forms at even very low temperature. NPA suggests that these structures could be best represented as $F^-(NgEF_3)^+$ and $F^-(NgEF)^+$. WBI values of Ng-E bonds are quite high ranging from 0.60 to 0.82 in $FNgEF_3$ whereas it is slightly lower in FNgEF ranging in between 0.38 and 0.70 with a gradual increment along Kr to Rn. From EDA, WBI and the bond lengths, the Xe/Rn-E bonds in $FNgEF_3$ and FNgEF might be termed as covalent bonds whereas Kr-E bond in FNgEF is a borderline case between partial and perfect covalent bonds. EDA shows that in F-Ng bonds, mainly ΔE_{elstat} contributes towards the total attraction implying their ionic character whereas in the Ng-E bonds of $FNgEF_3$ the contribution from ΔE_{orb} is the maximum showing their covalent character. In the Ng-E bonds of FNgEF, the partition into the charged fragments ($[FNg]^-$ + $[EF]^+$) gives ΔE_{elstat} as the major contributor but the consideration of the neutral fragments provides ΔE_{orb} as the most dominant term.

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Figures

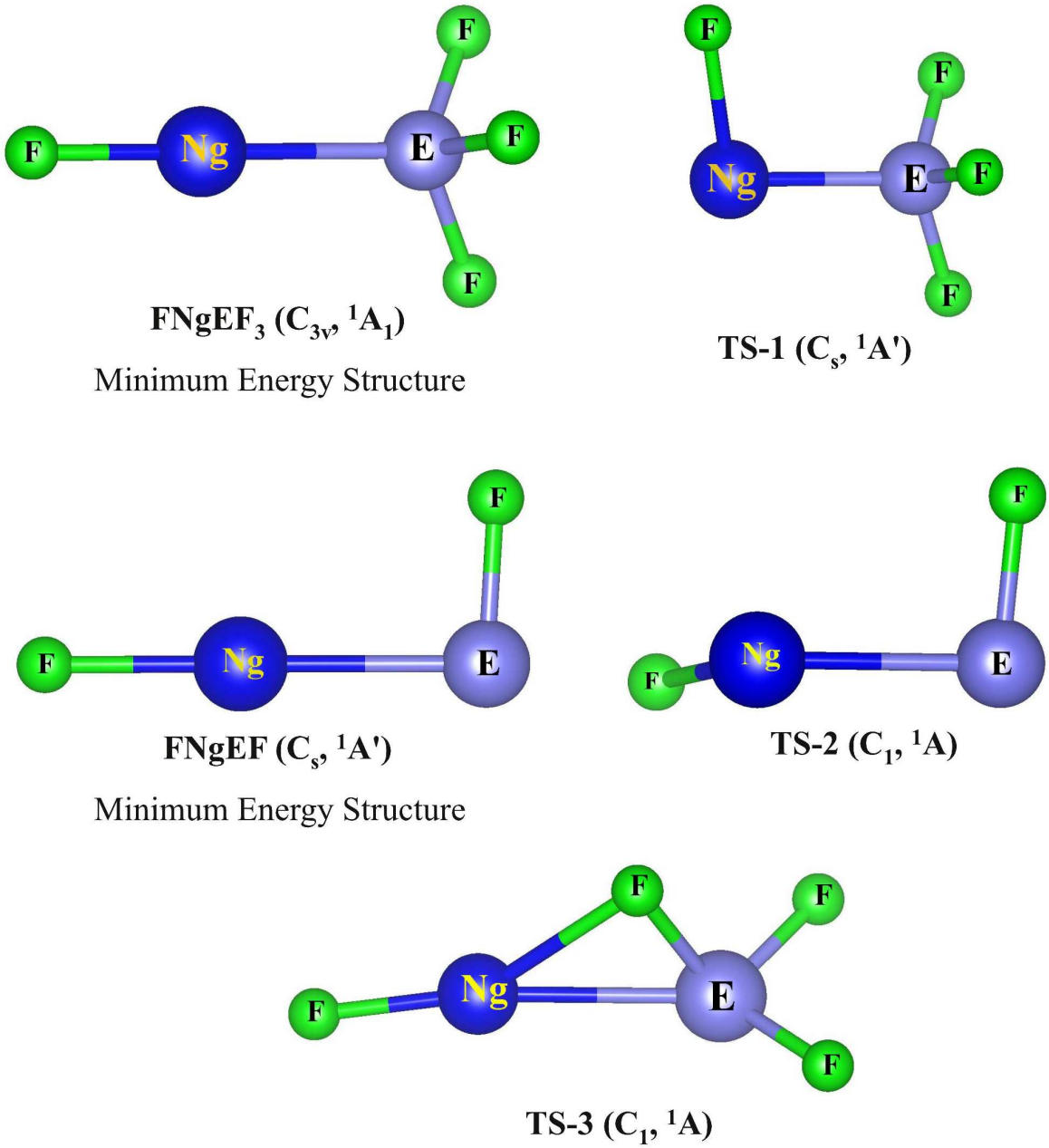


Fig. 1 Pictorial depictions of energy minimum structures and the transition states of $FNgEF_3$ and FNgEF clusters. Point groups along with their electronic states are given in parentheses. **TS-1** and **TS-2** are associated with the dissociation of $ENgEF_3$ and FNgEF producing Ng and EF_4 or EF_2. **TS-3** is associated with the dissociation of $ENgPbF_3$ producing NgF_2 and PbF_2.

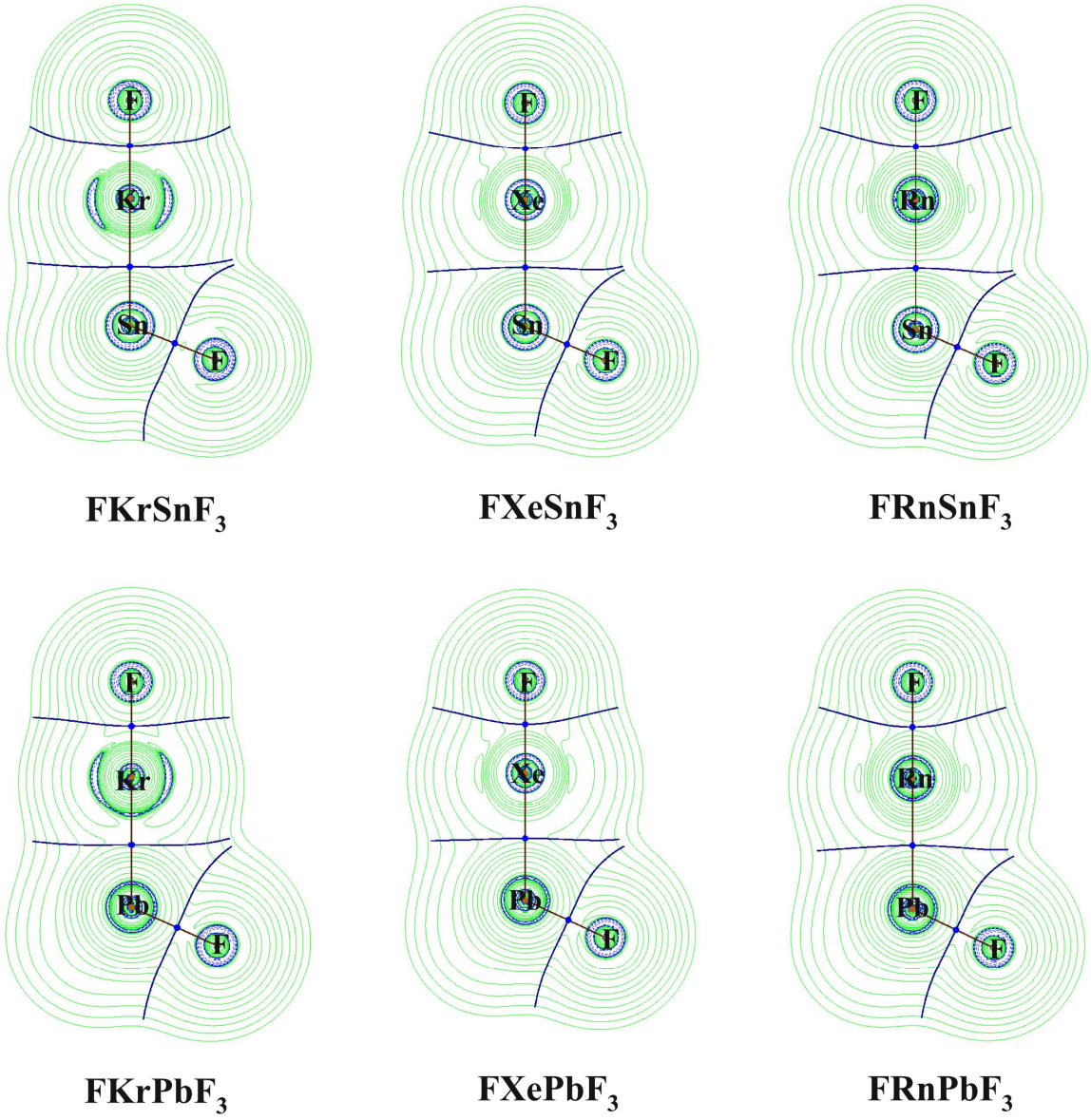


Fig. 2 Contour plots of the Laplacian of the electron density of $FNgSnF_3$ and $FNgPbF_3$ clusters at a particular plane computed at the MP2/def2-TZVPPD/WTBS level. (WTBS is used for Sn, Pb, Xe and Rn; Green colored region shows the area of $\nabla^2\rho(\mathbf{r})> 0$ whereas blue colored region shows the area of $\nabla^2\rho(\mathbf{r}) < 0$)

Tables

Table 1. ZPE corrected dissociation energy (D_0, kcal/mol), dissociation enthalpy (ΔH, kcal/mol) and free energy change (ΔG, kcal/mol) for different dissociation channels of $FNgSnF_3$ and FNgSnF clusters at the MP2/def2-TZVPPD level.

Processes	D_0			ΔH			ΔG		
	Kr	Xe	Rn	Kr	Xe	Rn	Kr	Xe	Rn
$FNgSnF_3 \rightarrow F + Ng + SnF_3$	7.6	31.8	46.1	8.2	32.4	46.7	-7.8	16.3	30.6
$FNgSnF_3 \rightarrow NgF_2 + SnF_2$	42.2	31.3	29.8	41.9	31.0	29.6	32.7	21.6	20.0
$FNgSnF_3 \rightarrow F^- + NgSnF_3^+$	135.5	150.9	158.5	135.9	151.3	159.0	128.0	143.3	151.1
$FNgSnF_3 \rightarrow Ng + SnF_4$	-105.3	-81.1	-66.7	-105.4	-81.2	-66.9	-111.3	-87.2	-72.8
$\Delta E^{\ddagger a}$	23.9	32.7	36.8						
$FNgSnF \rightarrow F + Ng + SnF$	24.7	40.0	49.7	25.3	40.6	50.3	11.5	26.7	36.4
$FNgSnF \rightarrow NgF_2 + Sn$	140.3	120.5	114.4	140.2	120.4	114.4	136.1	116.1	109.9
$FNgSnF \rightarrow F^- + NgSnF^+$	95.4	106.9	113.4	95.7	107.3	113.7	87.9	99.5	106.1
$FNgSnF \rightarrow Ng + SnF_2$	-105.4	-90.1	-80.4	-105.5	-90.2	-80.5	-111.5	-96.3	-86.6
$\Delta E^{\ddagger b}$	2.9	6.9	8.7						

$\Delta E^{\ddagger a}$ is the activation barrier for the process $FNgSnF_3 \rightarrow Ng + SnF_4$; $\Delta E^{\ddagger b}$ is the activation barrier for the process $FNgSnF \rightarrow Ng + SnF_2$

Table 2. ZPE corrected dissociation energy (D_0, kcal/mol), dissociation enthalpy (ΔH, kcal/mol) and free energy change (ΔG, kcal/mol) for different dissociation channels of $FNgPbF_3$ and FNgPbF clusters at the MP2/def2-TZVPPD level.

Processes	D_0			ΔH			ΔG		
	Kr	Xe	Rn	Kr	Xe	Rn	Kr	Xe	Rn
$FNgPbF_3 \rightarrow F + Ng + PbF_3$	-0.2	23.2	38.4	0.3	23.8	39.0	-14.8	8.0	23.2
$FNgPbF_3 \rightarrow NgF_2 + PbF_2$	1.7	-10.0	-10.7	1.1	-10.5	-11.1	-6.7	-19.1	-19.8
$FNgPbF_3 \rightarrow F^- + NgPbF_3^+$	149.0	163.7	172.0	149.4	164.1	172.4	142.1	156.3	164.6
$FNgPbF_3 \rightarrow Ng + PbF_4$	-76.9	-53.5	-38.3	-77.1	-53.6	-38.5	-82.2	-59.4	-44.3
$\Delta E^{\ddagger a}$	40.5	46.6	49.9						
$\Delta E^{\ddagger b}$	-a-	13.8	10.1						
$FNgPbF \rightarrow F + Ng + PbF$	26.2	41.1	50.7	26.8	41.7	51.3	13.1	27.9	37.5
$FNgPbF \rightarrow NgF_2 + Pb$	134.2	113.9	107.7	134.0	113.8	107.6	130.1	109.7	103.3
$FNgPbF \rightarrow F^- + NgPbF^+$	92.2	103.6	110.2	92.6	103.9	110.5	84.9	96.2	102.9
$FNgPbF \rightarrow Ng + PbF_2$	-95.4	-80.5	-70.9	-95.5	-80.6	-71.1	-101.5	-86.7	-77.1
$\Delta E^{\ddagger c}$	2.2	6.0	7.8						

$\Delta E^{\ddagger a}$ is the activation barrier for the process $FNgPbF_3 \rightarrow Ng + PbF_4$; $\Delta E^{\ddagger b}$ is the activation barrier for the process $FNgPbF_3 \rightarrow NgF_2 + PbF_2$; $\Delta E^{\ddagger c}$ is the activation barrier for the process $FNgPbF \rightarrow Ng + PbF_2$. -a- the transition state cannot be located.

Table 3. NPA charge on each atomic center (q_k, au) and WBI values of F-Ng and Ng-E bonds computed at the MP2/def2-TZVPPD level.

Clusters	q_k				WBI	
	F(Ng)	Ng	E	F(E)	F-Ng	Ng-E
$FKrSnF_3$	-0.81	+0.49	+2.55	-0.74	0.17	0.66
$FXeSnF_3$	-0.82	+0.69	+2.38	-0.75	0.20	0.79
$FRnSnF_3$	-0.83	+0.79	+2.31	-0.76	0.19	0.82
FKrSnF	-0.94	+0.23	+1.53	-0.82	0.06	0.43
FXeSnF	-0.92	+0.37	+1.37	-0.82	0.10	0.62
FRnSnF	-0.92	+0.44	+1.30	-0.82	0.10	0.70
$FKrPbF_3$	-0.69	+0.59	+2.28	-0.73	0.25	0.60
$FXePbF_3$	-0.74	+0.82	+2.14	-0.74	0.28	0.72
$FRnPbF_3$	-0.77	+0.94	+2.08	-0.75	0.27	0.73
FKrPbF	-0.94	+0.20	+1.57	-0.83	0.05	0.38
FXePbF	-0.926	+0.33	+1.42	-0.83	0.09	0.57
FRnPbF	-0.928	+0.411	+1.35	-0.83	0.09	0.66

Table 4. Electron density descriptors (au) at the bond critical points (BCP) of F-Ng and Ng-E bonds of $FNgEF_3$ and FNgEF compounds obtained from the wave functions generated at the MP2/def2-TZVPPD/WTBS level (WTBS for Sn, Pb, Xe and Rn atoms) taking optimized geometries at the MP2/def2-TZVPPD level.

Clusters	BCP	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$G(r_c)$	$V(r_c)$	$H(r_c)$	$G(r_c)/\rho(r_c)$	Class	r_{cov}	r_e
$FKrSnF_3$	F-Kr	0.104	0.281	0.101	-0.132	-0.031	0.971	B, C	1.73[a]/1.81[b]	2.03
	Kr-Sn	0.061	0.081	0.037	-0.053	-0.016	0.607	C	2.55[a]/2.57[b]	2.62
$FXeSnF_3$	F-Xe	0.090	0.290	0.099	-0.125	-0.026	1.100	W[c]	1.97[a]/1.95[b]	2.10
	Xe-Sn	0.054	0.041	0.024	-0.037	-0.013	0.444	C	2.79[a]/2.71[b]	2.76
$FRnSnF_3$	F-Rn	0.085	0.308	0.100	-0.123	-0.023	1.176	W[c]	2.07[a]/2.06[b]	2.16
	Rn-Sn	0.053	0.030	0.021	-0.035	-0.014	0.396	C	2.89[a]/2.82[b]	2.83
FKrSnF	F-Kr	0.062	0.233	0.065	-0.071	-0.006	1.048	W[c]	1.73[a]/1.81[b]	2.24
	Kr-Sn	0.049	0.108	0.036	-0.046	-0.010	0.735	C	2.55[a]/2.57[b]	2.68
FXeSnF	F-Xe	0.065	0.245	0.072	-0.083	-0.011	1.108	W[c]	1.97[a]/1.95[b]	2.27
	Xe-Sn	0.043	0.055	0.022	-0.030	-0.008	0.512	C	2.79[a]/2.71[b]	2.85
FRnSnF	F-Rn	0.065	0.240	0.072	-0.085	-0.013	1.108	W[c]	2.07[a]/2.06[b]	2.31
	Rn-Sn	0.043	0.042	0.019	-0.028	-0.009	0.442	C	2.89[a]/2.82[b]	2.93
$FKrPbF_3$	F-Kr	0.105	0.278	0.101	-0.132	-0.031	0.962	B, C	1.73[a]/1.81[b]	2.02
	Kr-Pb	0.049	0.064	0.026	-0.037	-0.011	0.531	C	2.62[a]/2.61[b]	2.75
$FXePbF_3$	F-Xe	0.096	0.305	0.107	-0.137	-0.030	1.115	W[c]	1.97[a]/1.95[b]	2.07
	Xe-Pb	0.049	0.054	0.024	-0.034	-0.010	0.490	C	2.86[a]/2.75[b]	2.85
$FRnPbF_3$	F-Rn	0.091	0.338	0.111	-0.137	-0.026	1.220	W[c]	2.07[a]/2.06[b]	2.12
	Rn-Pb	0.049	0.044	0.022	-0.033	-0.011	0.449	C	2.96[a]/2.86[b]	2.90
FKrPbF	F-Kr	0.059	0.225	0.061	-0.067	-0.006	1.034	W[c]	1.73[a]/1.81[b]	2.26
	Kr-Pb	0.047	0.117	0.037	-0.044	-0.007	0.787	C	2.62[a]/2.61[b]	2.80
FXePbF	F-Xe	0.064	0.241	0.070	-0.081	-0.011	1.094	W[c]	1.97[a]/1.95[b]	2.29
	Xe-Pb	0.041	0.066	0.023	-0.029	-0.006	0.561	C	2.86[a]/2.75[b]	2.92
FRnPbF	F-Rn	0.064	0.237	0.071	-0.083	-0.012	1.109	W[c]	2.07[a]/2.06[b]	2.32
	Rn-Pb	0.041	0.054	0.021	-0.028	-0.007	0.512	C	2.96[a]/2.86[b]	2.99

[a]the r_{cov} distance according to ref. 52 and [b]the r_{cov} distance according to ref. 53.

Table 5. EDA results of $FNgSnF_3$ and FNgSnF compounds (Ng = Kr-Rn) studied at the revPBE-D3/TZ2P//MP2/def2-TZVPPD level.

Systems	Fragments	ΔE_{int}	ΔE_{pauli}	ΔE_{elstat}	ΔE_{orb}	ΔE_{disp}
$FKrSnF_3$	$F^- + [KrSnF_3]^+$	-167.77	120.22	-186.20 (64.7%)	-101.63 (35.3%)	-0.15 (0.1%)
	$[FKr] + [SnF_3]$	-37.48	127.97	-40.66 (24.6%)	-123.88 (74.9%)	-0.91 (0.6%)
$FXeSnF_3$	$F^- + [XeSnF_3]^+$	-177.17	140.58	-211.40 (66.5%)	-106.23 (33.4%)	-0.12 (0.0%)
	$[FXe] + [SnF_3]$	-42.82	149.56	-50.16 (26.1%)	-141.19 (73.4%)	-1.03 (0.5%)
$FRnSnF_3$	$F^- + [RnSnF_3]^+$	-181.02	134.62	-216.61 (68.6%)	-98.92 (31.3%)	-0.11 (0.0%)
	$[FRn] + [SnF_3]$	-45.56	153.69	-53.76 (27.0%)	-144.35 (72.4%)	-1.14 (0.6%)
FKrSnF	$F^- + [KrSnF]^+$	-122.91	61.39	-127.74 (69.3%)	-56.37 (30.6%)	-0.19 (0.1%)
	$[FKr]^- + [SnF]^+$	-134.15	70.62	-126.23 (61.6%)	-77.87 (38.0%)	-0.68 (0.3%)
	$[FKr] + [SnF]$	-47.87	143.33	-41.87 (21.9%)	-148.65 (77.7%)	-0.68 (0.4%)
FXeSnF	$F^- + [XeSnF]^+$	-130.19	87.89	-149.70 (68.6%)	-68.26 (31.3%)	-0.13 (0.1%)
	$[FXe]^- + [SnF]^+$	-142.74	90.53	-144.64 (62.0%)	-87.89 (37.7%)	-0.75 (0.3%)
	$[FXe] + [SnF]$	-47.91	153.80	-46.51 (23.1%)	-154.46 (76.6%)	-0.75 (0.4%)
FRnSnF	$F^- + [RnSnF]^+$	-133.38	91.46	-157.14 (69.9%)	-67.57 (30.1%)	-0.13 (0.1%)
	$[FRn]^- + [SnF]^+$	-146.06	103.99	-156.12 (62.4%)	-93.09 (37.2%)	-0.84 (0.3%)
	$[FRn] + [SnF]$	-47.91	156.75	-49.00 (24.0%)	-153.92 (75.5%)	-0.84 (0.4%)

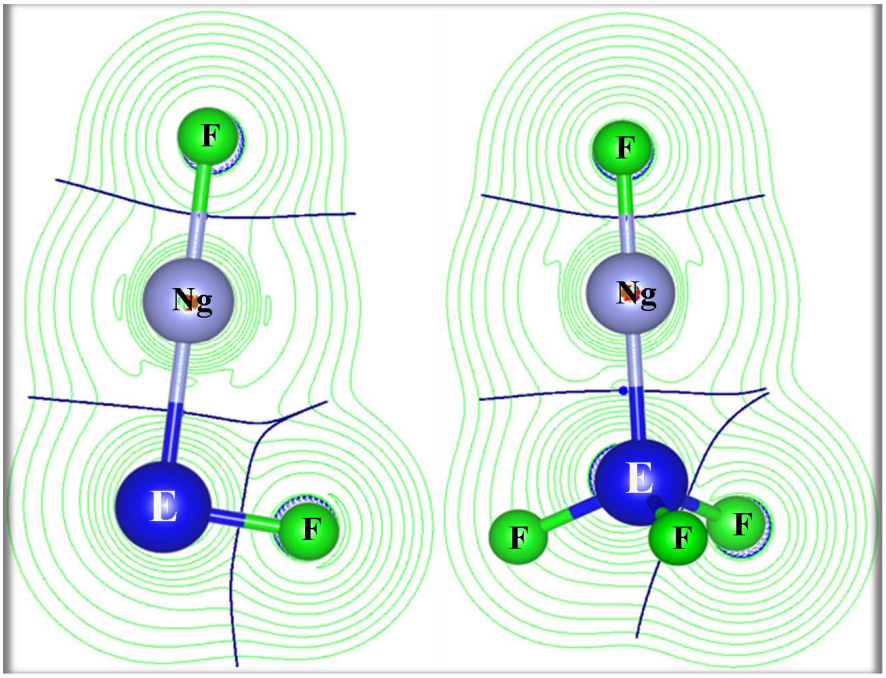
(The percentage values within the parentheses show the contribution towards the total attractive interaction $\Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp}$)

Table 6. EDA results of $FNgPbF_3$ and FNgPbF compounds (Ng = Kr-Rn) studied at the revPBE-D3/TZ2P//MP2/def2-TZVPPD level.

Systems	Fragments	ΔE_{int}	ΔE_{pauli}	ΔE_{elstat}	ΔE_{orb}	ΔE_{disp}
$FKrPbF_3$	$F^- + [KrPbF_3]^+$	-179.64	123.72	-181.40 (59.8%)	-121.81 (40.2%)	-0.15 (0.0%)
	$[FKr] + [PbF_3]$	-26.05	64.24	-15.55 (17.2%)	-73.97 (81.9%)	-0.77 (0.9%)
$FXePbF_3$	$F^- + [XePbF_3]^+$	-187.87	157.28	-219.76 (63.7%)	-125.28 (36.3%)	-0.12 (0.0%)
	$[FXe] + [PbF_3]$	-32.40	100.16	-30.25 (22.8%)	-101.43 (76.5%)	-0.88 (0.7%)
$FRnPbF_3$	$F^- + [RnPbF_3]^+$	-191.48	151.34	-227.03 (66.2%)	-115.67 (33.7%)	-0.11 (0.0%)
	$[FRn] + [PbF_3]$	-35.59	112.43	-36.54 (24.7%)	-110.49 (74.6%)	-0.99 (0.7%)
FKrPbF	$F^- + [KrPbF]^+$	-119.14	57.38	-122.02 (69.1%)	-54.30 (30.8%)	-0.19 (0.1%)
	$[FKr]^- + [PbF]^+$	-128.67	61.35	-119.92 (63.1%)	-69.46 (36.6%)	-0.64 (0.3%)
	[FKr] + [PbF]	-48.64	125.40	-35.41 (20.3%)	-137.99 (79.3%)	-0.64 (0.4%)
FXePbF	$F^- + [XePbF]^+$	-126.37	84.48	-144.40 (68.5%)	-66.31 (31.4%)	-0.14 (0.1%)
	$[FXe]^- + [PbF]^+$	-136.98	83.06	-140.58 (63.9%)	-78.73 (35.8%)	-0.72 (0.3%)
	[FXe] + [PbF]	-47.99	138.35	-40.87 (21.9%)	-144.76 (77.7%)	-0.72 (0.4%)
FRnPbF	$F^- + [RnPbF]^+$	-129.87	88.83	-152.45 (69.7%)	-66.12 (30.2%)	-0.13 (0.1%)
	$[FRn]^- + [PbF]^+$	-140.37	98.59	-154.30 (64.6%)	-83.83 (35.1%)	-0.83 (0.3%)
	[FRn] + [PbF]	-47.84	143.74	-45.03 (23.5%)	-145.71 (76.1%)	-0.83 (0.4%)

(The percentage values within the parentheses show the contribution towards the total attractive interaction $\Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp}$)

Graphical Abstract



The metastable FNgEF and $FNgEF_3$ (E = Sn, Pb; Ng = Kr-Rn) are the first reported neutral compounds possessing Ng-Sn and Ng-Pb covalent bonds.