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Towards Understanding the Stability of the N_5^+ -Containing Salts: The Role of Counterion

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The thermal stabilities of the $N_5^+M^-$ species ($M=Sb(OH)_6$, $Sb(OH)_4F_2$, AlF_6 , AlF_4 , BF_4 , $B(CF_3)_4$, PF_6 , AsF_6 and SbF_6) have been studied by means of density functional theory. The present calculations indicate that their thermal stabilities (represented by activation enthalpy, ΔH^\ddagger in kcal/mol) decrease in the order N_5^+ (47.2) > $N_5B(CF_3)_4$ (34.1) \approx N_5SbF_6 (31.6) \approx N_5AsF_6 (31.5) > N_5PF_6 (30.5) > N_5AlF_4 (27.1) \approx N_5BF_4 (27.1) > N_5AlF_6 (8.5). Only N_5SbF_6 has the small positive reaction enthalpy, Δ_rH . The thermal stability of N_5^+ salt depends on amounts of electron transfer from the counterion to N_5^+ in the reaction. The high electronegativity atoms or groups in the counterion are essential. Another crucial factor is bond strength between central ion and ligand. The studies of the $N_5Sb(OH)_4F_2$ isomers indicate that the OH rather than the fluorine ions in the axial coordination positions could stabilize the decomposition transition structure through partial dissociation of the Sb-OH bond, which is used to explain the reason why there is the obvious difference in decomposition activation enthalpy of the three isomers.

Introduction¹

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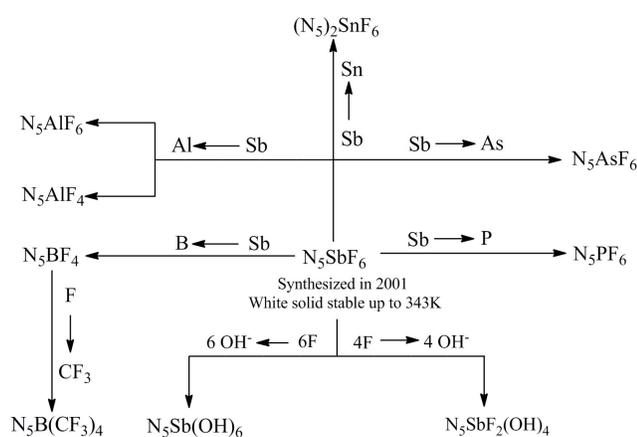
† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See

Polynitrogen compounds have received great attention as high energy density materials (HEDMs) for propulsion or explosive applications¹⁻⁷. Although a wealth of theoretical calculations have indicated that N_n ($n=4, 6, 8, 11$) systems may exist in acyclic forms or linear structures⁸⁻¹⁴, no such compounds have yet been successfully synthesized^{15, 16} because of their extreme instability. Inspiringly, N_5AsF_6 was successfully synthesized in 1999¹⁷ by Christe, which caused instant sensation and shocked the world. Indeed, N_5AsF_6 was considered as only the third known compound containing a stable homoleptic polynitrogen moiety, after N_2 isolated in 1772 by Rutherford and N_3^- first synthesized in 1890 by

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Curtius¹⁸. However, this white solid was only marginally stable at 22 °C and the damage it caused during low temperature Raman analysis revealed its instability. In 2001, N₅SbF₆¹⁹ was successfully obtained and proved to be more stable, decomposing only at above 70 °C.

To date, a total of 12 N₅⁺-containing salts have been synthesized^{17, 20, 21}, among which N₅SbF₆ is the most stable. In more than a decade, no further novel N₅⁺-containing salts with better thermal stability have been synthesized. Most published papers on N₅⁺-containing salts focused on their synthesis and properties, whereas there seems to have been limited research on the mechanism of their thermodynamic stability.^{22,23} Questions arise, such as why N₅SbF₆ has quite high thermal stability. In order to gain insight into the role of the central Sb atom as well as of the ligand F atoms in SbF₆⁻, other N₅⁺M⁻ salts (M= Sb(OH)₆, SbF₂(OH)₄, BF₄, B(CF₃)₄, AlF₄, AlF₆, AsF₆, and PF₆) (Scheme 1) have been selected for a comparative study.



Scheme 1. The strategy employed to study the root of the thermal stability of N₅SbF₆

Computational details

All calculations were performed using the Gaussian 09 package²⁴. Geometry optimizations of the starting structures were carried out at the M06-2X²⁵ level with the 6-311+G(d) basis set for B, C, N, F, Al and P atoms and SDD for other heavy metal atoms²². Each optimized structure was confirmed

as local energy minima on the potential-energy surface without imaginary frequencies. Note that M06-2X functional is very suitable to multi-nitrogen or pure nitrogen molecules according to previous studies²⁶.

Thermal stability is a key factor in evaluating the synthetic possibilities, and is closely related to the activation enthalpy of thermal dissociation (ΔH^\ddagger), which is determined by the transition state (TS). Calculations were performed to obtain the barrier heights in order to further discuss the relative stability of the relevant compounds. Activation enthalpy (ΔH^\ddagger) was calculated according to Eq. (1):

$$\Delta H^\ddagger = \Delta H_{\text{TS}} - \Delta H_{\text{R}} \quad (1)$$

where ΔH_{TS} and ΔH_{R} represent the enthalpies of the transition state and the reactant, respectively.

Results and discussion

Geometries of N₅⁺M⁻

The structure of N₅SbF₆ (see structure 2 in Fig. 1) was in good agreement with the reported data²³, which proved that our employed method was reliable. The obtained structures of N₅⁺-containing salts **1** to **11** are depicted in Fig. 1 and Fig. 2, in which compounds **3**, **4**, **10**, and **11a–11c** are the novel designed complexes indicated in Scheme 1. Selected bond lengths are listed in the figures.

The structural difference between the compounds **3**, **4** and **5–8** in Fig 1 is that they have the same ligand F but different central atoms, P, Al, As and Sn, respectively. The four compounds **2**, **11a**, **11b**, and **11c** in Fig. 2 have the same central atom Sb, but four or six of the fluorine atoms in N₅SbF₆ are substituted by OH. Compounds **11a**, **11b**, and **11c** are structural isomers with the same C₂ point group. They differ in the positions of the two fluorine atoms of the counter-ion. From the bond length shown in Fig. 1 and Fig. 2, it is noteworthy that the bond lengths in the isolated N₅⁺ unit are slightly longer than those in the other N₅⁺ salts, except in the case of structure **3** (N₅AlF₆), in which the N(1)-N(3) bond length (1.311 Å) is longer than that in the isolated N₅⁺ unit

(1.300 Å). These data showed that the central Al ion is strongly bonded with only four fluorine anions, while the other two fluorine ions are clearly away from the central Al ion through observation of the Al-F bond lengths of 1.784-1.961 Å in **3** (N_5AlF_6) and 1.664-1.727 Å in **4** ($N_5^+AlF_4^-$). These indicate the stronger Al-F bonds in the latter. Additionally, the Sb(6)-F(7) and Sb(6)-F(8) bond

with $N_5^+SbF_6^-$ results, N_5^+ with a high oxidation potential influences the Sb-F bond length. Moreover, the numbers of fluorine in counterion clearly influence electronegativity, which results in the difference of Sb-F bond length. These structural differences could reflect the variation of stability of the Sb-containing N_5^+ salts.

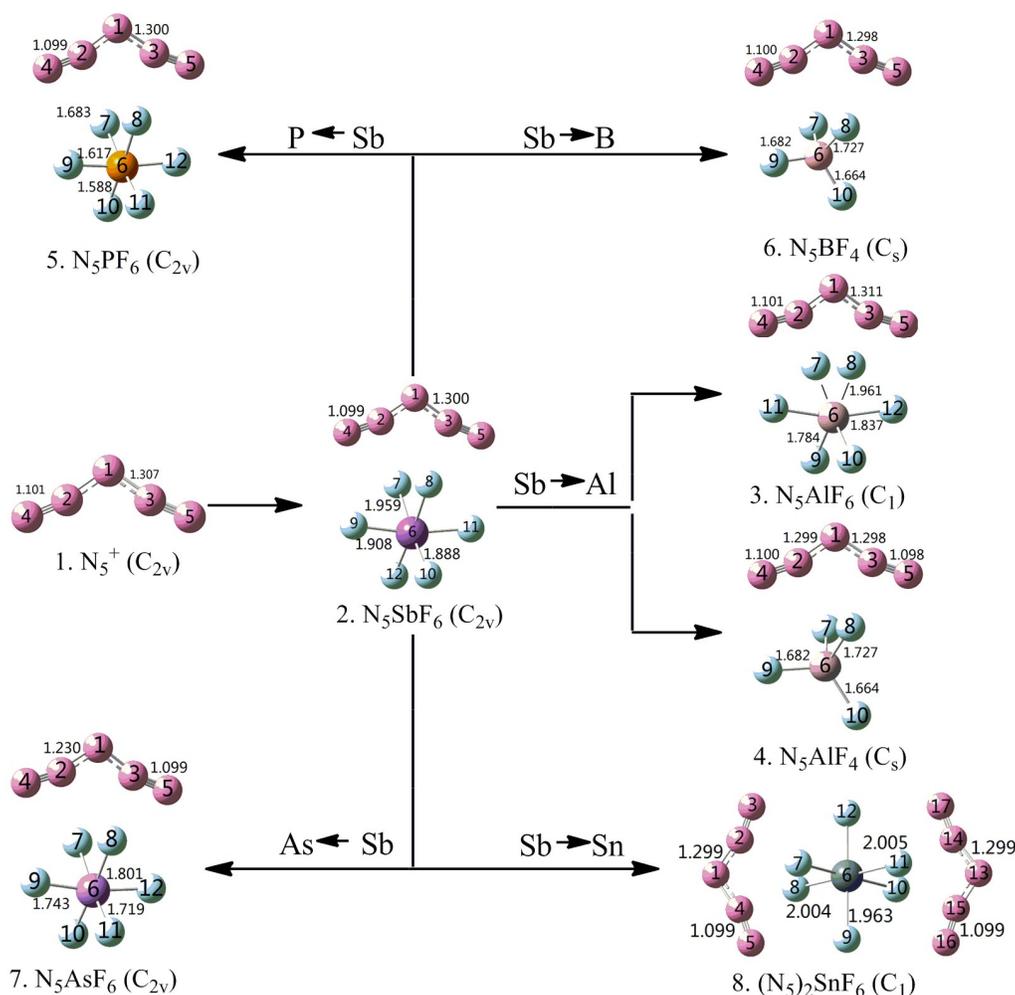


Fig. 1 Geometrical structures of the N_5^+ complexes in which the central atom Sb was substituted by Al, P, B, As and Sn with selected bond length shown in the structures.

lengths (1.959 Å) in N_5SbF_6 are clearly shorter than the corresponding Sb-F bond lengths (2.002 Å) in **11a**. The similar cases are also observed through comparison of the bond lengths between Sb(6)-F(9) in **2** and Sb(6)-F(7) in **11b**, Sb(6)-F(10) in **2** and Sb(6)-F(7) in **11c**. Combined

Decomposition mechanism of $N_5^+M^-$

For the thermal decomposition of isolated N_5^+ , the activation enthalpy was estimated to be 47.2 kcal/mol, indicating that N_5^+ has a good thermal stability. In addition, we explored the electronic spin reverse, i.e. the

states of N_5^+ are shown in Fig. 3. As the reaction coordinate changes, there is a crossover point between the two states of N_5^+ . The actual thermal dissociation process should initiate from the reactant to the crossover point; thereafter, this process continues along the triplet potential energy surface of

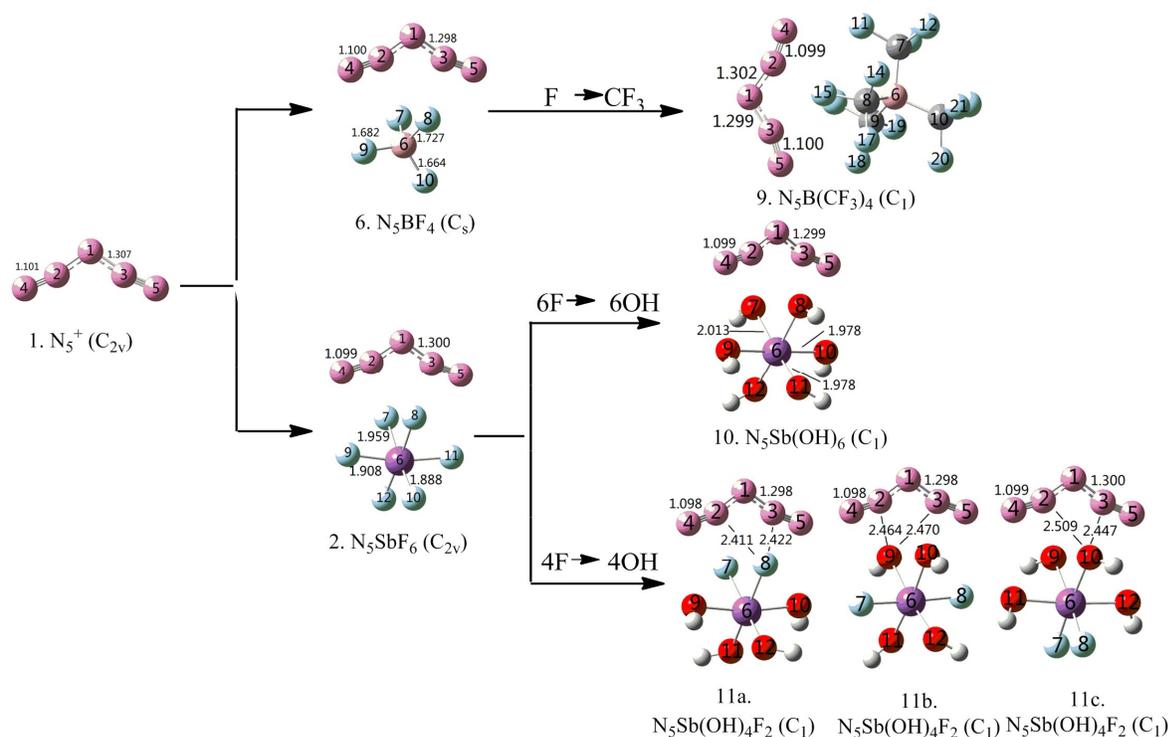


Fig. 2 Geometrical structures of the N_5^+ complexes in which the ligand F was substituted by OH and CF_3 in N_5SbF_6 and N_5BF_4 with selected bond length shown in the structures.

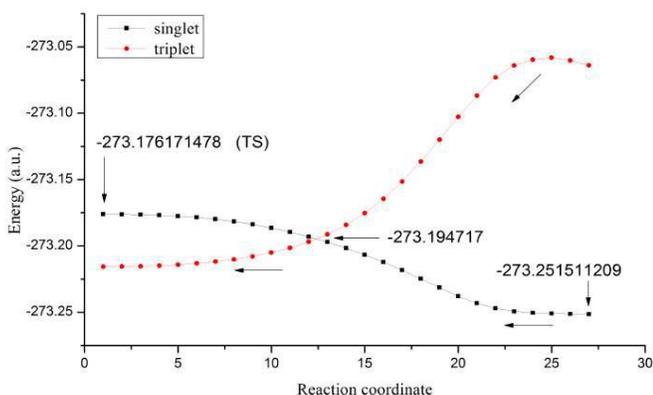


Fig. 3 The energy curves for both the triplet and singlet states of N_5^+ during its dissociation process.

photodissociation and coupling of thermal cracking events that may occur during the thermal dissociation of the N_5^+ cation. The energy curves for both the triplet

N_5^+ to the products, the linear triplet N_3^+ and N_2 , as suggested by Nguyen⁵. The energy difference between the crossover point and the reactant was estimated to be ca. 35.6 kcal/mol. The above analysis indicates that the N_5^+ is thermally stable in the gas phase.

When N_5^+ is combined with M^- , the decomposition mechanism of N_5^+ should be similar to that in its isolated case. Table 1 showed NPA charge plus of all nitrogen atoms of N_5^+ salts in the reactant and their decomposition transition states.

From the table 1 we can find the partially negative charges (ca. 0.03 ~ 0.05 e) transfer from the counterion to N_5^+ of the salt in the reactant states. N_5AlF_6 has the most amount of charge transfer. These results discover the intermolecular essentially electrostatic interaction between M^- and N_5^+ .

Moreover, this interaction can further induce N_5^+ decomposition into N_2 and more oxidative N_3^+ , which results in more negative charge transfer from the counterion to the $N_2 \cdots N_3^+$ complex, seen in table 1. Ultimately, N_3^+ can capture one F anion of the counterion to form N_3F product. (Seen in **supporting materials**) Thus, the stronger the ability of M^- to retain electrons in the decomposition reaction, the more stable the $N_5^+M^-$ species is.

Table 1. NPA charge plus of all nitrogen atoms of N_5^+ salts and their decomposition transition states

Compound	N_5AlF_4	N_5AlF_6	N_5AsF_6	N_5SbF_6
qN (a)	0.958	0.756	0.961	0.964
qN (b)	0.783	0.386	0.786	0.785
Compound	N_5BF_4	$N_5B(CF_3)_4$	N_5PF_6	$N_5Sb(OH)_6$
qN (a)	0.952	0.970	0.959	0.941
qN (b)	0.744	0.789	0.778	0.624
Compound	11a	11b	11c	
qN (a)	0.940	0.952	0.942	
qN (b)	0.664	0.718	0.645	

qN(a) represents the NPA charge plus of all nitrogen atoms of each salt in the reactant state. qN(b) represents the NPA charge plus of all nitrogen atoms of each salt in the decomposition transition state.

The role of the central atom in stabilizing $N_5^+M^-$

To study the role of the central atom in stabilizing N_5^+ , we replaced Sb in N_5SbF_6 with Al, B, P and As. Table 2 lists the thermal decomposition activation enthalpy (ΔH^\ddagger) and reaction enthalpy ($\Delta_r H$) of the N_5^+ -containing salts. Calculations show that the thermal stability is in the order $N_5B(CF_3)_4 \approx N_5SbF_6 \approx N_5AsF_6 > N_5PF_6 > N_5AlF_4 \approx N_5BF_4 > N_5AlF_6$. One hand, the larger volume of the counterion favors improvement of the thermal stability of the salt. On the other hand, the present reactivity order is clearly explained through the amount of the negative charge transfer from the counterion to N_5^+ during the reaction procedure, seen table 1. An interesting case is found for N_5AlF_6 , where

the two fluorine ions in the equatorial positions are obviously separated from the central Al ion. The partially dissociated Al-F bond suggests that the two F ions could be not strongly bound by the central Al ion so that F ion tends to shift to N_5^+ , which could promote decomposition of the N_5^+ cation. The shorter Al-F bond in N_5AlF_4 indicates stronger interaction between Al and F, which is relatively more difficult to be broken in the decomposition reaction. This is why AlF_4^- should be preferred over AlF_6^- to stabilize N_5^+ . Both activation and reaction enthalpies calculations indicated that N_5AlF_4 is more stable than N_5AlF_6 , which is consistent with

the conclusion that the bond strength between the central atom and the ligand is significant for N_5^+ stability. The more strongly bound F anion in SbF_6^- and AsF_6^- has a relatively less chance for dissociation of F anion so as to approach N_5^+ , which leads to their higher thermal stability. Moreover, comparison of thermodynamics between N_5BF_4 and $N_5B(CF_3)_4$ salts shows that group $B(CF_3)_4^-$ with higher electronegativity should be preferred to stabilize N_5^+ . Note that the reaction enthalpy of N_5SbF_6 is only small positive among the salts, which shows that the salt has not only dynamic stability but thermodynamic one. Though N_5PF_6 has the barrier height close to N_5SbF_6 , more exothermic decomposition reaction of N_5PF_6 could be one of the reasons why the salt is not stable enough in room temperature.

Table 2. Activation enthalpy (ΔH^\ddagger) and reaction enthalpy ($\Delta_r H$) of N_5^+ complexes (in kcal/mol)

Compound	N_5AlF_4	N_5AlF_6	N_5AsF_6	N_5SbF_6
ΔH^\ddagger	27.1	8.5	31.5	31.6
$\Delta_r H$	-4.7	-56.9	-2.5	+1.2
Compound	N_5BF_4	$N_5B(CF_3)_4$	N_5PF_6	
ΔH^\ddagger	27.1	34.1	30.5	
$\Delta_r H$	-17.5	-0.2	-10.9	

The role of fluorine atoms in stabilizing $N_5^+M^-$

All known stable N_5^+ -containing salts have F atoms in their counterions. To better study the role of fluorine ion in

stabilizing $N_5^+M^-$, the OH group was selected to substitute F because OH and F are isoelectronic and moreover, oxygen and fluorine have the closest electronegativities among all single atoms. The calculated activation energy of $N_5Sb(OH)_6$ is 19.1 kcal/mol, which is much lower than that of N_5SbF_6 (30.3 kcal/mol).

This large thermal stability difference between $N_5Sb(OH)_6$ and N_5SbF_6 should originate from the different electronegativity of fluorine and OH. Fluorine has higher electronegativity than OH, and for the same central atom Sb, the bond strength of Sb-F is greater than that of Sb-OH. Thus, electrons are more favorably bound in SbF_6^- and less charge is transferred to N_5^+ to accelerate its dissociation, compared with the case in $N_5Sb(OH)_6$. Considering that fluorine has the highest electronegativity of any single atom, we may reasonably infer that fluorine is indispensable in stabilizing N_5^+ -containing salts if the ligand is a single atom. Additionally, seeking other potential functional groups with high electronegativity contained in the counterion might be helpful to improve the stability of the N_5^+ salts.

There are six fluorine ions in SbF_6^- , and a further question that arises is which of these plays a major role in stabilizing N_5^+ . In order to ascertain the position of the functional fluorine ions, we studied the $N_5Sb(OH)_4F_2$ isomers - **11a**, **11b**, and **11c**. Calculations show that the relative enthalpy of the above isomers is 0.0 (**11a**), 0.8 (**11b**), and 0.3 (**11c**) kcal/mol in their reactant states. However, the relative enthalpy is 0.0 (**11a**), 7.7 (**11b**), and -0.6 (**11c**) kcal/mol in their transition states. The order of their activation barriers is **11b** (28.6) > **11a** (21.7) > **11c** (20.8). These data clearly show that the stability variation among the isomers should be attributed to the difference of their total energies in the transition states. NBO calculations show that in the decomposition transition structure of **11b**, there are the smallest charge amounts transferred from the counterion to N_5^+ decomposition structure, which corresponds to the highest reaction barrier height among the decomposition reactions of the three isomers. Actually, the two fluorine atoms in the axial coordination positions of **11b** are relatively not favorable to

stabilize the transition structure. Comparison of the transition structures of the three isomers discovers that the two OH ions in the axial coordination positions of **11a** and **11c** should be better selection to stabilize the transition structures with respect to lower barrier heights. The case should be attributed to the stronger Sb-F than Sb-OH bonds so that the former is relatively more difficult to be ruptured to form F ion. Thus, the bound F has no enough negative charge on itself to stabilize the formed N_3^+ fragment in the transition structure. In **11a** and **11c**, one of the axial coordination OH anions could stabilize the N_3^+ fragment in the transition structure through Sb-OH partial bond dissociation. The remaining two fluorine ions should also contribute to stabilize N_5^+ , whether they are close to or far away from the formed N_5^+ fragment. This is consistent with the conclusion of **11a** and **11c** having almost the same barrier heights.

Conclusions

Density functional theory studies have indicated that the interaction between M^- ion and the N_5^+ cation causes thermal instability in the latter. Strong bonding between the central atom and the ligand atom in the counter anion is significant for holding ligand anion in M^- so as to favour N_5^+ stability. Among the simple single-atom ligands, fluorine is the best choice due to its highest electronegativity. In addition, fluorine atoms in specific positions show greater contributions to control the N_5^+ decomposition. We hope that our theoretical work could provide a useful contribution for future synthesis of the novel and more complex anions to stabilize N_5^+ .

Acknowledgements

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The role of counterion of N_5^+ -containing salts in stabilizing N_5^+ cation was studied by means of density functional theory.

