Novel Cationic Selenium-Cluster Nitride Species $[Se_nN]^+$ ($n = 1-11$) Formed by Laser Ablation of a Se Target in the Presence of N_2

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Abstract: Nitride cations of selenium clusters $[Se_nN]^+$ ($n = 1-11$) were readily produced by laser ablation of a selenium disk that was surrounded by a trace amount of nitrogen seeded in helium and followed by supersonic expansion into a high vacuum. Even at high nitrogen partial pressures, the cluster mononitride cations were found to be essentially the only nitride products in the whole size range we studied. The exception was $[Se_3N_2]^+$, which is known to be a stable five-membered ring with seven π electrons. We propose that, in the laser-ablation plasma, the selenium clusters with $n > 2$ take on a chain conformation, and that the N species links the two ends of the selenium chains, thus forming stable mononitride cations of the cyclic selenium clusters. Their stability is supported by the results of ab initio calculations (at both B3LYP/6-31+G* and MP2/6-31+G* levels) and of mass-selected cluster-ion photodissociation experiments.

Keywords: ab initio calculations · cluster compounds · laser chemistry · nitrides · selenium

Introduction

Growing interest in selenium–nitrogen chemistry has been directed towards exploring the possibly unusual structures and properties of Se–N compounds, as compared with S–N compounds.[1–3] Although the highly explosive molecule Se_4N_4 has been known for many years, its laboratory synthesis was not accomplished until 1992.[1, 4] In 1994, a new synthesis of Se_4N_4 was described, and crystals of this compound were obtained directly from solution.[5] With the development of the experimental methods, many binary Se–N cations and ternary selenium-nitrogen-halides have been synthesised. The binary selenium-nitrogen cations include the five-membered seven π- and six π-electron systems, $[Se_3N_2]^+$ and $[Se_3N_2]^{2+}$, which can be obtained by direct oxidation of Se_4N_4.[1, 6] In SO_2 solution, the dication $[Se_3N_2]^{2+}$ rapidly reaches equilibrium with $[SeN]^+$ and $[Se_2N]^+$, according to the ^{77}Se NMR spectroscopic data. Most work thus far has focused on the synthesis of new Se–N chlorides. For example, the ternary compound Se_2NCl_3 was prepared by the action of tris(trimethylsilyl)amine on a suspension of selenium tetrachloride in boiling dichloromethane.[7] The subsequent reaction of Se_2NCl_3 with the strong Lewis acid gallium trichloride led to the formation of $[Se_2NCl_2]^+[GaCl_4]^-$. Similar compounds such as $[Se_3N_2Cl]^+Cl^-$,[4] Se_2NBr_3,[8] Se_2NCl_5,[8] $[Se_2NCl_6]^-$,[8] $[(SeCl)_2N]^+$[7, 9a] and $[(SeCl_2)_2N]^+[AsF_6]^- \cdot MeCN$[9b] have been successfully synthesised by using different chemical methods. Most recently, a method that involved microwave-discharge, followed by deposition onto a 12 K substrate and detection by IR absorption, was employed by Andrews and co-workers for producing and studying selenium–nitrogen species.[10]

Although significant progress has been made in the area of selenium–nitrogen chemistry, almost all the Se–N compounds synthesised so far are limited to, at most, four selenium atoms. An emerging issue is the synthesis, stability and structural propensity of large selenium-cluster nitrides. This is important in view of the fact polymeric $(SN)_x$ is a well-known superconductor. In addition, doping selenium with nitrogen may be a useful method for tailoring its semiconducting properties for electronic and photonic applications. During our studies of selenium clusters, we have recently discovered that nitride cations of selenium clusters in a wide range of sizes can be produced with remarkable ease by laser ablation of a selenium disk in the presence of nitrogen, followed by supersonic expansion.[11] In this paper, we report the synthesis of nitride cations of selenium clusters by this method. We identified the molecular masses of these clusters by reflectron time-of-flight mass spectrometry (TOFMS). Combining the laser-photodissociation experiments and ab initio calculations, the special affinity of the selenium-cluster cations for nitrogen atoms can be understood. We also discuss possible mechanisms for the formation of the nitride cations of selenium clusters.

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Results and Discussion

Formation of nitride cations of selenium clusters: A typical time-of-flight mass spectrum of selenium-cluster cations is shown in Figure 1 (top). Selenium-cluster cations Se_n^+ with $n > 11$ can be easily identified by their characteristic intensity distribution.[11–13] Notice that these clusters were generated without adding N_2 to the carrier gas. However, careful mass analysis of the mass spectrum in Figure 1 (top) shows that nitride cations of selenium clusters $[Se_nN]^+$ are still apparent for $n = 2-5$. The only source of nitrogen atoms appears to be from adsorption onto the selenium sample, because the cluster-nitride signals decrease with an extended period of laser ablation. It is remarkable that, even with a trace amount of N_2 on the selenium sample, the cluster-nitride cations can still be formed by laser ablation. This clearly shows that selenium does indeed have a special affinity for nitrogen. When N_2 was introduced into the carrier gas, the cluster-nitride cation signals start to soar. Figure 1 (bottom) shows the mass spectrum when the fraction of N_2 in the carrier gas is 20%; this seems to be close to the optimum condition for the formation of nitride cations of selenium clusters. For small clusters ($n \leq 5$), the intensity of the nitride cations is even greater than that of the corresponding bare cluster cations. In the larger cluster size range ($n \geq 6$), the relative intensity of the nitride cations decreases. It is worth noting that, when the fraction of N_2 in the carrier gas increases, only the mononitride cations show a dramatic increase. Perhaps the only exception is the formation of the dinitride cation $[Se_3N_2]^+$. The fact that $[Se_3N_2]^+$ is known to be stable as a seven π-electron system on a five-membered ring suggests that the nitride cations of selenium clusters we produced have a certain amount of stability. In other words, for selenium clusters, the mononitride cations are likely to be more stable than multinitride cations. Kinetic effects may also be important in the formation of the mononitride cations of selenium clusters.

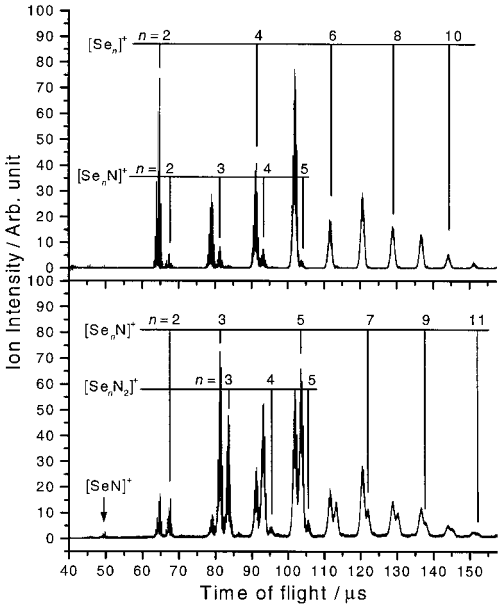

Figure 1. Top: Time-of-flight mass spectrum of selenium-cluster cations with no N_2 added to the He carrier gas. Bottom: Time-of-flight mass spectrum with 10% N_2 added to the He carrier gas. Otherwise, the spectra were recorded under the same conditions.

When we replaced N_2 with NH_3 as the source of nitrogen atoms, no nitride cations of selenium clusters were produced. Because both NH_3 and N_2 can provide N atoms in laser-ablation plasma; this result implies that N_2 molecules rather than N atoms are important in the reaction that leads to the formation of the nitride cations of selenium clusters. One possible mechanism involves the activation of N_2 by the excited selenium-cluster cations in the laser-ablation plasma. The excited selenium-cluster cations may prefer a chain configuration and, when they react with N_2, the two chain ends are likely to be connected by one nitrogen atom after the splitting off the other nitrogen atom. This naturally explains why the mononitride cations of the selenium clusters are the predominant products in the reaction.

We also recorded the mass spectrum of the cluster anions by reversing the polarity of our detection system. While we observed a series of bare selenium-cluster anions Se_n^- ($n = 1-13$) under the same reaction conditions as in Figure 1 (bottom), no nitride anions of selenium clusters were detected. This is understandable if one notices that most Se–N compounds synthesised so far involve selenium nitride cations.[4–9] From a chemical point of view, N is more likely to be linked to positively charged selenium atoms. Our ab initio calculations, below, also support this inference.

Photodissociation of mass-selected cluster cations: Photodissociation experiments were carried out on mass-selected $[Se_nN]^+$ ($n = 1-5$). $[SeN]^+$ and $[Se_2N]^+$ cannot be dissociated with a single photon at 342 nm; this indicates high Se–N bond strengths in these two species. Considering that $[SeN]^+$ and $[Se_2N]^+$ are valence-isoelectronic to N_2 and CO_2, respectively, their photo-stability is evident. Photodissociation difference mass spectra of $[Se_3N]^+$, $[Se_4N]^+$ and $[Se_5N]^+$ at 342 nm are presented in Figure 2. In general, all the photofragments we observed involved the breakage of Se–Se bonds, and the channel of N elimination is completely closed. In fact, the photofragments (see Figure 2) are mostly smaller nitride cations of selenium clusters such as $[SeN]^+$, $[Se_2N]^+$, and so on. This constitutes more support for the photo-stability of these species. The photodissociation-difference mass spectrum of $[Se_5N]^+$ (Figure 2 (bottom)) is contaminated by Se_5^+ due to the low resolution of our mass gate; nevertheless, this does not really alter our conclusion above. Based on our previous work, [11] we believe that the daughters Se_2^+ and Se_3^+ (Figure 2 (bottom)) are mostly from photodissociation of the contaminant Se_5^+.

The fragments shown in Figure 2 are all from one-photon dissociation processes, because the photon energy at 342 nm is sufficient to drive the photodissociation events. For example, the formation of $[SeN]^+$ from the photodissociation of $[Se_3N]^+$ is found to have a threshold at ~420 nm as shown in Figure 3. The fact that we did not observe any of the fragments associated with N ejection at 342 nm suggests that the threshold of this dissociation channel is much higher.

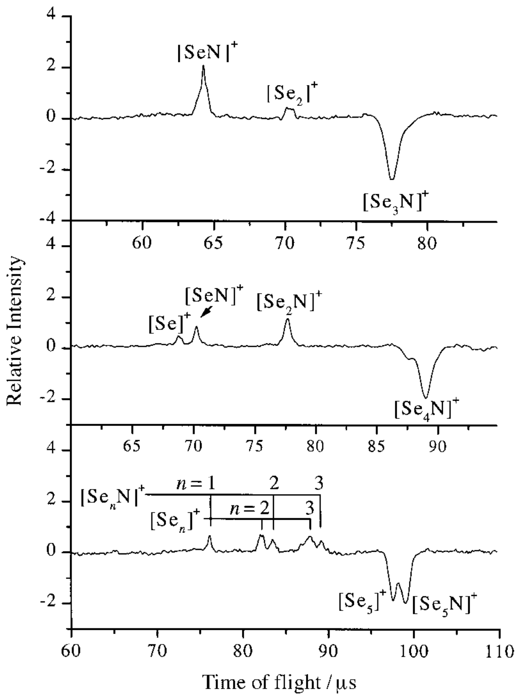

Figure 2. Photodissociation-difference mass spectra for top: $[Se_3N]^+$, middle: $[Se_4N]^+$ and bottom: $[Se_5N]^+$ at 342 nm. The laser fluence used was 5 mJ cm^{-2}.

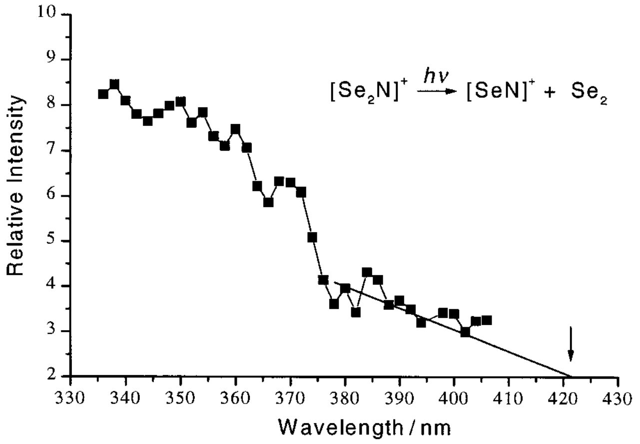

Figure 3. Photodissociation-yield curve of the fragment cation SeN^+ from mass-selected $[Se_3N]^+$ as a function of photon energy.

Ab initio calculations: Further evidence for the special affinity of selenium-cluster cations for nitrogen is obtained from our ab initio calculations. Although some theoretical investigations were carried out on Se–N systems, most previous calculations concerned either neutral or ternary species.[4, 6, 8–10] In our calculations, the ground-state geometry of $[Se_nN]^+$ ($n = 1-5$) was fully optimised at both the B3LYP and the MP2 level for comparison by using the GAUSSIAN98 program package.[14] The basis set of 6-31 + G* was used in all the calculations reported in this paper. Both levels of theory gave similar results in terms of the structural aspects (see Table 1) and, therefore, only the results of the B3LYP calculations are reported here. To test the relativistic effect on the results of our calculations, we also performed B3LYP geometry optimisations of the two structural isomers **IIIa** and **IIIb** of $[Se_3N]^+$ by using Stuttgart-type quasi-relativistic pseudopotentials for Se.[15] The pseudopotential basis set was augmented with polarisation functions ($\zeta = 0.315$) used in 6-31 + G*. These testing calculations give only slight changes in the calculated structural parameters when compared with those from the all-electron calculations. The changes in the bond lengths and bond angles are within 0.03 Å and 1°, respectively. The energy difference changes from 24.29 to 29.07 kcal mol^{-1}. Clearly, these calculations suggest that the relativistic effect is not important in calculating the structures and relative stabilities of the $[Se_nN]^+$ species.

The optimised structures for $[Se_{1-5}N]^+$ are shown in Figures 4 and 5, and the energies associated with these structures are listed in Table 1. The calculated bond lengths, charge distributions and bond angles for all the structures are also indicated in Figures 4 and 5. The bond of $[Se{\equiv}N]^+$ (1.58 Å) is significantly shorter than the single bond Se–N (1.86 Å).[8, 16] This is consistent with the similar triple bond in the valence-isoelectronic N_2. $[Se_2N]^+$ is found to have a nearly perfect linear structure ($D_{\infty h}$) in much the same way as in its

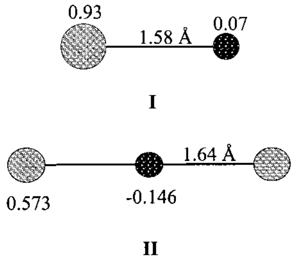

Figure 4. Calculated structures of $[SeN]^+$ (**I**) and $[Se_2N]^+$ (**II**) (B3LYP/6-31 + G*).

Table 1. Calculated energies of $[Se_nN]^+$ ($n = 1-5$) (B3LYP or MP2/6-31 + G*)

Species		Structure	Energies (B3LYP) (Hartree)	Relative energies (kcal mol^{-1})	Energies (MP2) (Hartree)	Relative energies (kcal mol^{-1})
$[SeN]^+$	**I**	linear	−2453.7314904	–	−2451.9462431	–
$[Se_2N]^+$	**II**	linear	−4853.2259427	–	−4849.7469101	–
$[Se_3N]^+$	**IIIa**	cyclic	−7252.6340149	0	−7247.4409058	0
	IIIb	linear	−7252.5953050	24.29	−7247.4098402	19.49
$[Se_4N]^+$	**IVa**	cyclic	−9652.0635779	0	−9645.1704192	0
	IVb	linear (U-shape)	−9652.0265109	23.26	−9645.1504598	12.52
	IVc	(S-shape)	−9652.0234982	25.15	−9645.1434276	16.93
	IVd	(W-shape)	−9652.0202651	27.18	−9645.1382845	20.16
$[Se_5N]^+$	**V**	cyclic	−12051.487326	–	−12042.9018743	–

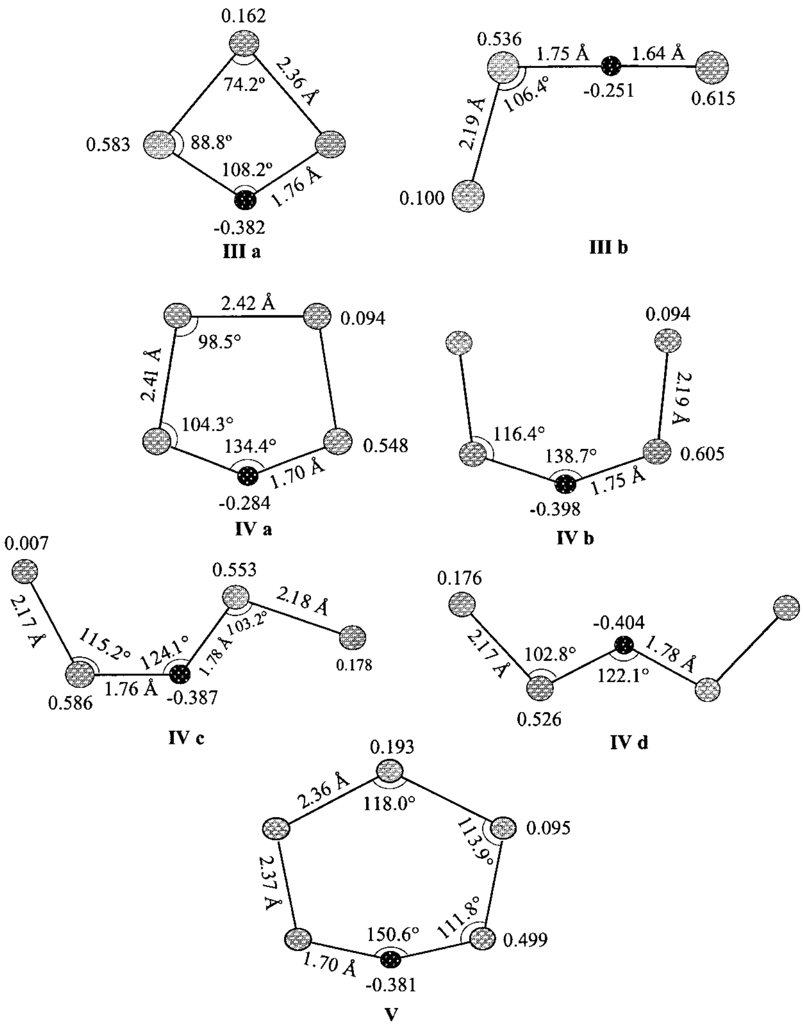

Figure 5. Calculated structures of $[Se_3N]^+$ (**IIIa** and **b**), $[Se_4N]^+$ (**IVa–d**) and $[Se_5N]^+$ (**V**) (B3LYP/6-31+G*). Note that the most stable structures for $[Se_{3-5}N]^+$ are monocyclic rings.

valence-isoelectronic partner CO_2. Owing to the special electronic structure, together with the strong Se–N bonds, $[Se_2N]^+$ is also a rather stable species. Our calculations also give the bond-dissociation energies of $[SeN]^+$ (9.75 eV: $[SeN]^+ \rightarrow Se^+ + N$) and $[Se_2N]^+$ (6.18 eV: $[Se_2N]^+ \rightarrow [SeN]^+ + Se$), which are close to the bond dissociation energies of N_2 (9.8 eV)[17] and CO_2 (5.5 eV)[17], respectively. At 1.64 Å, the Se=N bond in $[Se_2N]^+$ is somewhat longer than the Se≡N triple bond, but shorter than the Se–N single bond. From the results of our calculations presented above, $[SeN]^+$ and $[Se_2N]^+$ are very stable species; this explains why no photodissociation occurred for these species at 342 nm and why they are the dominant daughters from the photodissociation of $[Se_{3-5}N]^+$. In fact, these species were also found to be abundant in the neutralisation–re-ionisation mass spectrum of a five-membered ring compound $[F_3C(CSeNSeC)CF_3]^+$-$[SbCl_6]^-$, in which the ring contains $[Se_2N]^+$ and an unsaturated C=C bond.[18]

From Table 1, one can conclude that the most stable structures for $[Se_{3-5}N]^+$ are mono-cyclic rings (C_{2v}) (structures **IIIa**, **IVa** and **V** in Figure 5). For $[Se_3N]^+$ and $[Se_4N]^+$, some possible linear structures were also calculated (see **IIIb**, **IVb**, **IVc** and **IVd** in Figure 5). Although the four-membered ring $[Se_3N]^+$ (**IIIa**) may have great ring strain, this is balanced by its favourable aromatic six π-electron system. A similar strained ring system is the isoelectronic, neutral species Se_2N_2.[10] The five-membered ring $[Se_4N]^+$ (**IVa**) and six-membered ring $[Se_5N]^+$ (**V**) are also found to be quite stable. This is especially true for $[Se_5N]^+$ due to its aromatic ten π-electron ring system. In $[Se_3N]^+$ and $[Se_5N]^+$, all the Se–Se bond lengths are ~2.36 Å; this is very close to the Se–Se bond length in pure Se_6 ($r_{Se-Se} = 2.34$ Å)[19] and in the Se_6 unit of $[NEt_4]^+_4[(Se_5)_2Se_6(Se_7)_2]^{2-}$ ($r_{Se-Se} = 2.375$ Å).[20] However, due to the ring strain in the $[Se_3N]^+$ ring and the tendency to satisfy the aromatic $4n+2$ rule, the Se–N bond lengths in $[Se_3N]^+$ are substantially greater (0.06 Å) than those in $[Se_5N]^+$. For the same reason, the Se-N-Se angle in $[Se_5N]^+$ is significantly larger than that in $[Se_3N]^+$.

We noticed that the nitrogen atom carries a partial negative charge in all the structures for which we did calculations, and that the positive charge is mainly localised on the two neighbouring Se atoms. In principle, the mononitride cation rings of the selenium clusters can be considered as a juxtaposition of this $[Se\text{-}N\text{-}Se]^+$ unit and the remaining part, Se_{n-2}, which is almost neutral. Interestingly, the bond lengths are rather insensitive to the variation in bond angles for both units, and this bonding flexibility largely accounts for the stability of the monocyclic rings.

Conclusion

In summary, we have produced novel nitride cations of selenium clusters by combination of laser ablation and supersonic expansion. N_2 was used as the reagent, and its atomic constituents, N atoms, are shown to be easily incorporated into the selenium-cluster cations. Mononitride cations of selenium clusters are found to be the dominant products. Small nitride cations of selenium clusters within the size range of $n = 1-5$ were mass-selected for photodissociation. The results of the photodissociation experiment demonstrate the photo-stability of the mononitride cations of selenium clusters. Ab initio calculations on $[Se_nN]^+$ ($n = 1-5$) have been performed to fully optimise their structures at both the B3LYP level and the MP2 level by using the 6-31 + G* basis set. The calculations show that $[Se_2N]^+$ has a very stable linear structure, while the most stable structures for $[Se_nN]^+$ ($n = 3-5$) are monocyclic rings (C_{2v}). The possible formation mechanism of the nitride cations of selenium clusters has been considered, and it may involve the activation of the nitrogen bond by the two ends of the highly excited linear selenium-cluster cations.

Experimental Section

The main apparatus for the present experiments was described previously,[11] and thus only parts relevant to the present experiments are given here. A schematic of our nozzle source is shown in Figure 6. Selenium powder (100 mesh; 99.999 %) was compressed, at an hydraulic pressure of ~0.8 GP, into a disk ~1.3 cm in diameter on a sample holder. The sample disk was then mounted 15 mm downstream from the exit of the pulsed valve (General Valve). Driven by a step motor, the sample disk rotates on each laser pulse to expose the fresh surface during the laser-ablation experiments. The second harmonic of a Nd:YAG laser was focused on a 0.5 mm diameter spot on the selenium disk to generate selenium-cluster cations. The optimum ablation-laser energy for producing the cluster cations was found to be ~20 mJ per pulse: average cluster sizes become smaller at higher laser energies, while cluster signal intensities become weaker at lower laser energies. The laser-ablated plume was entrained into the helium carrier gas plus a fraction of N_2 (partial pressure: 1–2 psi), with a total pressure of ~10 psi. The clusters were formed in a channel 2 mm in diameter and 3.5 cm long and cooled through He expansion into a high vacuum. The cluster beam then travelled 14 cm down to the extraction region of the reflectron time-of-flight mass spectrometer (RTOFMS).

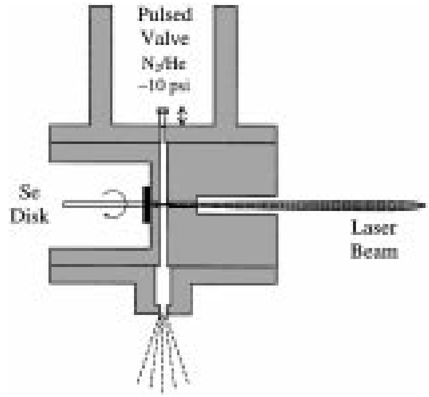

Figure 6. Schematic diagram of the nozzle used for generating the nitride cations of selenium clusters $[Se_nN]^+$. Carrier gas pressure: 10 psi; Gas pulse width: 800 µs.

The cluster cations in the extraction region were extracted vertically by a two-stage accelerator by using a high-voltage pulse with an amplitude of 1120 V and a width of 25 µs. After extraction, the cluster cations were steered by a pair of horizontal and a pair of vertical deflection plates. The voltages on these plates were set at +800 V and −100 V, respectively. All the cluster cations were reflected by the reflectron (VR1 = 650 V and VR2 = 1050 V) and finally detected by a dual-plate microchannel detector (MCP).

For photodissociation experiments, a two-plate mass gate equipped with a high-voltage pulser (normally high at +900 V) was used to select the desired cluster cations. After arriving at the turn-around region of the reflectron, the mass-selected cluster cations were irradiated with a collimated beam from a dye laser. The parent and nascent daughter cations were re-accelerated by the reflectron electric field and detected by the MCP detector. The dye laser for photodissociation was pumped by an XeCl excimer laser (Lambda Physik LPX210i/LPD3002). Several dyes, p-Terphenyl, DMQ and BBQ, were used to cover the spectral region between 310–405 nm.

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[1] I. C. Tornieporth-Oetting, T. M. Klapöthe in *Advances in Molecular Structure Research*, *Vol. 3* (Eds.: M. Hargittai, I. Hargittai), JAI, New York, **1997**, pp. 287–311.

[2] M. Björgvinsson, H. W. Roesky, *Polyhedron* **1992**, *10*, 2353–2370.

[3] P. F. Kelly, A. M. Z. Slawin, D. J. Williams, J. D. Woollins, *Chem. Soc. Rev.* **1992**, 245–252.

[4] a) J. Siivari, T. Chivers, R. S. Laitinen, *Inorg. Chem.* **1993**, *32*, 4391–4395; b) J. Siivari, T. Chivers, R. Laitinen, *Angew. Chem.* **1992**, *104*, 1539–1540; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1518–1519.

[5] H. Folkerts, B. Neumuller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1994**, *620*, 1011–1015.

[6] E. G. Awere, J. Passmore, S. White, *J. Chem. Soc. Dalton Trans.* **1993**, 299–310.

[7] R. Wollert, A. Höllwarth, G. Frenking, D. Fenske, H. Goesmann, K. Dehnicke, *Angew. Chem.* **1992**, *104*, 1216–1218; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1251–1253.

[8] C. Lau, B. Neumuller, W. Hiller, M. Herker, S. F. Vyboishchikov, G. Frenking, K. Dehnicke, *Chem. Eur. J.* **1996**, *2*, 1373–1378.

[9] M. Broschag, T. M. Klapötke, I. C. Tornieporth-Oetting, P. S. White, *J. Chem. Soc. Chem. Commun.* **1992**, 1390–1391.

[10] L. Andrews, P. Hassanzadeh, D. V. Lanzisera, G. D. Brabson, *J. Phys. Chem.* **1996**, *100*, 16667–16673.

[11] X. Yang, Y. H. Hu, S. H. Yang, M. M. T. Loy, *J. Chem. Phys.* **1999**, *111*, 7837–7843.

[12] J. Becker, K. Rademann, F. Hensel, *Z. Phys. D* **1991**, *19*, 233–235.

[13] K. Nagaya, T. Hayakawa, M. Yao, H. Endo, *J. Non-Cryst. Solids* **1996**, *205*, 807–810.

[14] Gaussian 98, Revision A.1, Gaussian Inc., Pittsburgh, Pennsylvania, **1998**.

[15] A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, *80*, 1431–1441.

[16] M. Broschay, T. M. Klapötke, A. Schulz, P. S. White, *Inorg. Chem.* **1993**, *32*, 5734–5738.

[17] *CRC Handbook of Chemistry and Physics*, 75th Ed., (Ed.: D. R. Lide), CRC, Boca Raton, **1994**, pp. **9**-55, **9**-66.

[18] K. B. Borisenko, M. Broschag, I. Hargittai, T. M. Klapötke, D. Schroder, A. Schulz, H. Schwarz, I. C. Tornieporth-Oetting, P. S. White, *J. Chem. Soc. Dalton Trans.* **1994**, 2705–2712.

[19] *CRC Handbook of Chemistry and Physics*, 75th Ed., (Ed.: D. R. Lide), CRC, Boca Raton, **1994**, p. **9**-22.

[20] J. Dietz, U. Muller, V. Muller, K. Dehnicke, *Z. Naturforsch. Teil B* **1991**, *46*, 1293–1299.

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