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Pyridine *N*-selenide radical cations: synthesis, characterization, neutralization, and ion–molecule reactions in the gas phase

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Abstract

Cyanogen *N*-selenide radical cations, $\text{NCCNSe}^{+\cdot}$, react efficiently with neutral pyridine producing the elusive pyridine *N*-selenide radical cations. The structure of these new distonic ions has been established by high energy collisional activation (CA), neutralization–reionization mass spectrometry, and associative ion–molecule reactions with nitric oxide, methyl isocyanide, pyridine- d_5 , dimethyl disulfide, and dimethyl diselenide. These experiments have been performed in a new hybrid mass spectrometer having the sectors–quadrupole–sectors configuration. (Int J Mass Spectrom 184 (1999) 39–47) © 1999 Elsevier Science B.V.

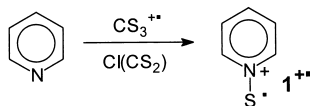
Keywords: Pyridine *N*-selen(ox)ide; Collisional activation; Neutralization–reionization; Ion–molecule reactions

1. Introduction

Whereas the stability and the chemistry of *N*-oxides derived from pyridine and related compounds are well established [1], the *N*-sulfide and the *N*-selenide analogues are still elusive compounds. This is in keeping with the general instability of N–S or N–Se containing compounds as compared to their N–O analogues [2]. Actually, N–S and N–Se compounds, in contrast to their N–O analogues, contain a coordinate covalent bond between elements of the fifth and sixth groups in which the element bearing the formal negative charge is less electronegative than the element bearing the formal positive charge. The electronegativities of nitrogen, oxygen, sulfur, and selenium amount, indeed, to 3.0, 3.5, 2.5, and 2.4, respectively.

Recently, we have produced and identified the molecular ions of pyridine *N*-sulfide **1** in the gas phase of our tandem mass spectrometer [3]. These radical cations were generated by ionized sulfur transfer from $\text{CS}_3^{+\cdot}$ radical cations to neutral pyridine under chemical ionization (CI) conditions using carbon disulfide as the CI reagent gas (Scheme 1). The so-produced ions were characterized by comparing their collision induced fragmentations with those observed for the isomeric mercaptopyridine–pyridine–thione systems. The $\text{CS}_3^{+\cdot}$ radical cations have also been used to realize efficiently the transfer of ionized sulfur to neutral nitriles generating the corresponding ionized nitrile *N*-sulfides [4]. Ion–molecule reactions between $\mathbf{1}^{+\cdot}$ radical cations and various neutral reagents (nitric oxide, pyridine- d_5 , dimethyl disulfide, and dimethyl diselenide) have also been performed in order to ascertain the *N*-sulfide structure and to probe the chemical reactivity of these new distonic ions [3].

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Scheme 1.

These experiments were conducted in a new hybrid tandem mass spectrometer presenting the sectors–quadrupole–sectors configuration [5].

Because of the use of collision induced neutralization, the first step of the neutralization–reionization mass spectrometry (NRMS) methodology [6], neutral pyridine *N*-sulfide has been proved to be a stable and consequently observable molecule in the gas phase.

Cyanogen *N*-selenide radical cations, $\text{N} \equiv \text{C} - \text{C} \equiv \text{N}^+ - \text{Se}^\cdot$, $2^{+\bullet}$, are readily generated by dissociative ionization of 3,4-dicyano-1,2,5-selenadiazole, **3** [7]. The associative interaction between those ions, $2^{+\bullet}$, and neutral nitriles has allowed the production of a series of nitrile *N*-selenide radical cations, $\text{R}-\text{C} \equiv \text{N}^+ - \text{Se}^\cdot$ [8]. The connectivities of these ions and the stabilities of the corresponding neutrals were established by collisional activation (CA) and NRMS, respectively.

In the present article we report on the first generation of pyridine *N*-selenide radical cations, $4^{+\bullet}$, by ionized selenium transfer reaction from $\text{N} \equiv \text{C} - \text{C} \equiv \text{N}^+ - \text{Se}^\cdot$, $2^{+\bullet}$, to neutral pyridine in the gas phase of a mass spectrometer. The structure of the so-produced radical cations was elucidated following collisional activation and ion–molecule reactions with several neutral reagents such as nitric oxide, methyl isocyanide, pyridine- d_5 , dimethyl disulfide (DMDS), and dimethyl diselenide (DMDS₂).

2. Experimental

All the spectra were recorded on a large scale tandem mass spectrometer (Micromass AutoSpec 6F) combining six sectors of $E_1B_1 \odot E_2 \odot E_3B_2 \odot E_4$ geometry (E stands for electric sector, B for magnetic sector, \odot for the collision cells used in this work) [9]. General conditions were 8 kV accelerating voltage, 200 μA trap current (in the electron impact mode), 1

mA (in the chemical ionization mode), 70 eV ionizing electron energy, and 200 °C ion source temperature. The solid samples were introduced with a direct insertion probe, whereas the liquid samples were injected in the ion source via a heated (180 °C) septum inlet.

NR spectra were recorded by scanning the field of the third electric sector and collecting the ions in the fifth field-free region with an off-axis photomultiplier detector.

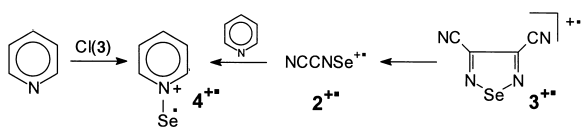
The installation of an rf-only quadrupole collision cell inside the instrument between E_2 and E_3 has also been reported elsewhere [5]. In this configuration, the neutralization cell is replaced by a demagnification lens. Briefly, the experiments utilizing the quadrupole consist of the selection of a beam of fast ions (8 kV) with the three first sectors ($E_1B_1E_2$), the retardation of these ions to ~ 5 eV, and the reaction with a reagent gas in the cell (the pressure of the reagent gas is estimated to be around 10^{-3} Torr). After reacceleration to 8 kV, all the ions present in the quadrupole are separated and mass measured by scanning the field of the second magnet. More interestingly, the high energy CA spectra of the ions present in the quadrupole can be recorded by a linked scanning of the fields of the last three sectors (EBE) (resolved mode) or a conventional scanning of the field of the last electric sector after mass selection with the second magnet.

All the samples used were commercially available, except for 2-selenopyridine, **5**, and methyl isocyanide (CH_3NC) which were prepared according to [10] and [11], respectively.

3. Results and discussion

The chemical ionization of pyridine using 3,4-dicyano-1,2,5-selenadiazole, **3**, as the CI reagent gas leads to the formation of several different ionic species. The main ions of interest generated under these conditions are the ionic adducts $[\text{C}_5\text{H}_5\text{N}, \text{Se}]^{+\bullet}$ (m/z 159, ^{80}Se containing compound). These ions are formally produced by $\text{Se}^{+\bullet}$ addition to neutral pyridine (Scheme 2).

As expected from previous work [7,8], $\text{NCCNSe}^{+\bullet}$



Scheme 2.

radical cations (m/z 132), $2^{+\bullet}$, are the principal reactive ions for this Se $^{++}$ transfer reaction. This is readily established by an ion–molecule reaction performed in the quadrupolar collision cell. Indeed, if a beam of the m/z 132 ions is mass selected and decelerated to about 5 eV before entering the cell containing neutral pyridine, ion–molecule $[\text{C}_5\text{H}_5\text{N}, \text{Se}]^{+\bullet}$ products are readily generated (Scheme 2, Fig. 1).

The most nucleophilic center of the pyridine ring being the nitrogen atom, the expected structure for this $[\text{C}_5\text{H}_5\text{N}, \text{Se}]^{+\bullet}$ adduct is the pyridine *N*-selenide structure, **4**. Further indirect support is also found in the transfer of an ionized methylene [12] from distonic ions such as $\cdot\text{CH}_2\text{OCH}_2^+$ or the transfer of an ionized sulfur [3] from $\text{CS}_3^{+\bullet}$ to neutral pyridine, which have been thoroughly studied in recent years, indicating that the resulting ions are, respectively, the molecular ions of pyridine *N*-methylide or the molecular ions of pyridine *N*-sulfide, **1**. Other experimental data are nevertheless required in order to confirm this hypothesis.

Collisional activation and mass-selected ion–molecule reactions are powerful tools for the elucidation of ion structures. CA has become the standard method

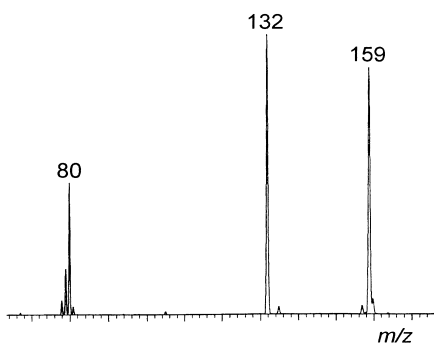


Fig. 1. Mass spectrum (B scan) of the ions produced by reaction of $\text{NCCNSe}^{+\bullet}$ ions, $2^{+\bullet}$ (m/z 132), and neutral pyridine in the Qcell.

for ions characterization [13]. In some instances, however, this technique fails in the differentiation of isomeric ions because collision-induced fragmentations are preceded by isomerization [14]. In such cases, ion–molecule reactions with an appropriate neutral reagent have allowed the distinction between isomers [14]. We therefore decided to use a combination of both techniques to accurately define the structure of the $[\text{C}_5\text{H}_5\text{N}, \text{Se}]^{+\bullet}$ ions.

3.1. Metastable ion, collisional activation, and neutralization–reionization experiments

The unimolecular decompositions (metastable ion spectrum, MI) of $5^{+\bullet}$ radical cations are the loss of HCN (m/z 132, 10% of the most intense signal at m/z 78), the loss of HSe \cdot radicals (m/z 78, 100%), and the loss of CSe (m/z 67, 15%). The fragments of the metastable $[\text{C}_5\text{H}_5\text{N}, \text{Se}]^{+\bullet}$ ions are identical with those observed MI spectrum of $4^{+\bullet}$ radical cations with an additional loss of selenium atoms (m/z 79) leading to the formation of ionized pyridine. Branching ratios: m/z 132 (loss of HCN, less than 1% of the most intense signal at m/z 78), m/z 79 (loss of Se atoms, 14%), and m/z 67 (loss of CSe, 14%).

The collision-induced dissociations of $[\text{C}_5\text{H}_5\text{N}, \text{Se}]^{+\bullet}$ ions generated in the quadrupolar cell and the fragmentations of the corresponding ions prepared in the CI source are identical, indicating that the ions formed in both cases have the same structure. The CA spectrum of $4^{+\bullet}$ (m/z 159) is compared in Fig. 2 to the CA spectrum of the molecular ions of 2-selenopyridine, **5**. Both spectra are quite similar except for the signal at m/z 79 corresponding to the loss of a selenium atom. This fragmentation, characteristic of the *N*-selenide structure, constitutes the base peak of the CA spectrum of $4^{+\bullet}$ [Fig. 2(a)] and is not expected for the reference ions $5^{+\bullet}$. This fragmentation is, moreover, in keeping with the Stevenson–Audier rule, the ionization energy of pyridine (9.26 eV) being lower than the ionization energy of selenium (9.75 eV) [15].

The interpretation of the NR spectra of $4^{+\bullet}$ and $5^{+\bullet}$ is not straightforward. The NR spectrum of $4^{+\bullet}$ [Fig. 3(a)] features, indeed, a weak recovery signal (RS)

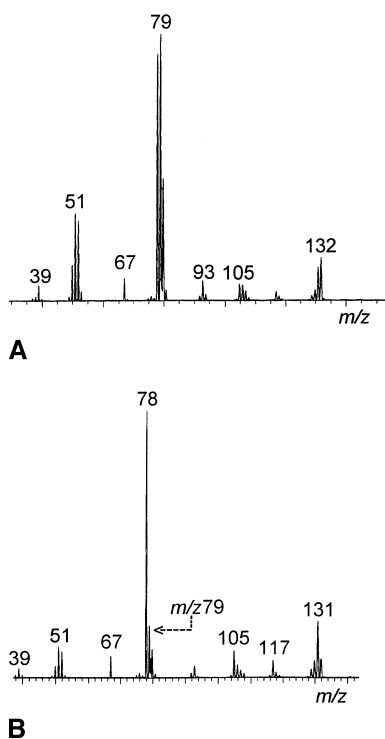


Fig. 2. (a) CA (O_2) spectra of the m/z 159 ions produced in the quadrupolar cell during the interaction between $NCCNSe^{+}$ ions, 2^{+} , and pyridine; (b) direct electron ionization of 2-selenopyridine 5^{+} .

which could indicate that neutral **4** is a stable molecule in the gas phase, however, the observed fragments are quite similar to those present in the NR spectrum of 5^{+} [Fig. 3(b)]. Moreover, starting from 4^{++} or 5^{+} , the NR spectra differ significantly from the corresponding CA spectra. That may be the result of reionization of neutrals produced in unimolecular dissociations (vide supra): m/z 92 (reionization of neutrals produced during the metastable generation of m/z 67 ions), m/z 81 (reionization of SeH radicals), and m/z 80 (reionization of selenium atoms) in the specific case of 4^{++} . The very intense signal at m/z 80 observed in both spectra may also be due to reionization of Se atoms lost from the neutrals during the flight between the reionization and the neutralization cells. The situation is complicated, moreover, by the fact that selenopyridine **5** is a tautomerizable compound and can exist in tautomeric forms in the gas phase. It is possible that the occurrence of an intense

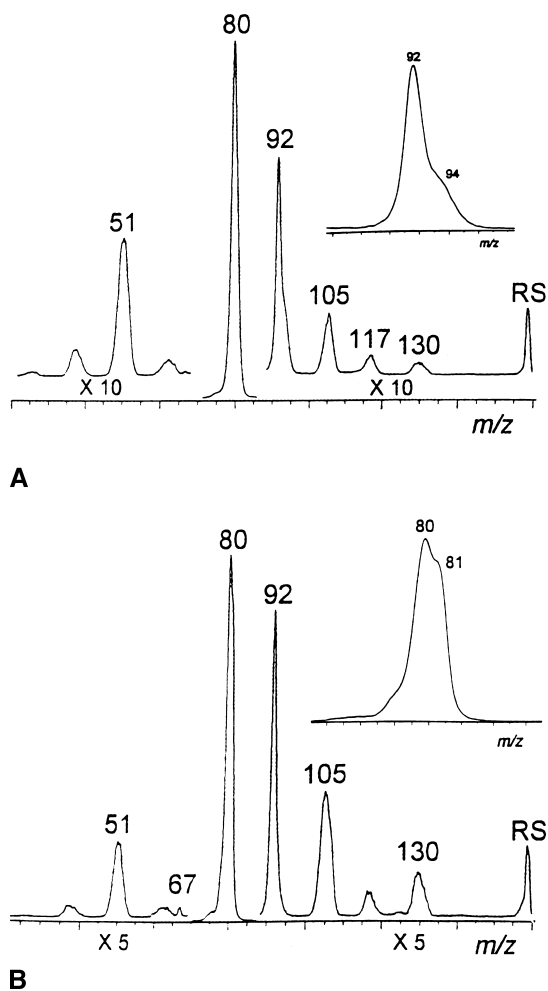
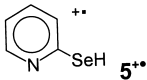
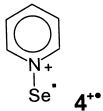


Fig. 3. NR (Xe/O_2) mass spectra of m/z 159 ions produced (a) by chemical ionization (**3** as the reagent gas) of pyridine, and (b) by electron ionization of 2-selenopyridine 5^{+} . The insets show extended views of the m/z 86–98 (a) and the m/z 74–85 (b) regions.

signal at m/z 80 in the NR spectrum of 5^{+} arises from the neutralization of ionized pyridineselenone (vide infra, structure **9**).

We nevertheless suggest that neutral **4** could be a stable molecule in the gas phase, and that part of the recovery ions could be the molecular ions of pyridine *N*-selenide, 4^{++} . Indeed, the observation of m/z 94 ions (NSe^{+}) only in the NR spectrum of 4^{++} [inset of Fig. 3(a)] could support the presence of 4^{++} after the reionization step because this fragmentation is not likely to be a decomposition of neutral **4**. An NR/CA

Table 1
Products of ion–molecule reactions between $[C_5H_5N, Se]^{+}$ isomers and neutral reagents

Neutrals	 5⁺		 4⁺	
NO \cdot	NO $^+$	(<i>m/z</i> 30)	NO $^+$ SeNO $^+$	(<i>m/z</i> 30) (<i>m/z</i> 110)
CH $_3$ NC	No reaction		CH $_3$ NCSe $^{+}$ Pyr $^{+}$	(<i>m/z</i> 121) (<i>m/z</i> 79)
Pyridine- d_5	Pyr- d_5^{+} Pyr- d_5 H $^+$	(<i>m/z</i> 84) (<i>m/z</i> 85)	Pyr- d_5^{+} Pyr- d_5 H $^+$ [Pyr - d_5 + Se] $^{+}$	(<i>m/z</i> 84) (<i>m/z</i> 85) (<i>m/z</i> 164)
DMDS	DMDS $^{+}$ [5 $^{+}$ + CH $_3$ S] $^+$	(<i>m/z</i> 94) (<i>m/z</i> 206)	DMDS $^{+}$ [DMDS + Se] $^{+}$ [4 $^{+}$ + CH $_3$ S] $^+$	(<i>m/z</i> 94) (<i>m/z</i> 174) (<i>m/z</i> 206)
DMDSe	DMDSe $^{+}$ [5 $^{+}$ + CH $_3$ Se] $^+$	(<i>m/z</i> 190) (<i>m/z</i> 254)	DMDSe $^{+}$ [4 $^{+}$ + CH $_3$ Se] $^+$ [DMDSe + Se] $^{+}$	(<i>m/z</i> 190) (<i>m/z</i> 254) (<i>m/z</i> 270)

experiment (collisional activation of the survivor ions) could be suitable to solve this problem but, for sensitivity reasons, such an experiment is not feasible in this case.

3.2. Ion–molecule reactions with nitric oxide, methyl isocyanide, and pyridine- d_5

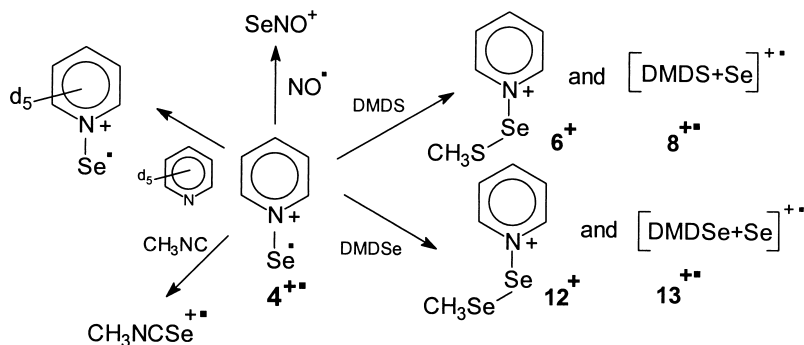
Distonic ions are recognized to be very efficient reagents for the transfer of charged odd-electron groups to neutral molecules [12,14b,16]. For instance, the electron ionization of oxirane leads to \cdot CH $_2$ OCH $_2^+$ radical cations [17] and these distonic ions readily react with several neutral reagents by CH $_2^+$ transfer [12].

Weiske et al. [18] have shown, using Fourier transform ion cyclotron resonance that the interaction between \cdot CH $_2$ - X $^+$ - CH $_3$ distonic ions and nitric oxide (NO \cdot) leads to the formation of CH $_2$ NO $^+$ ions. Therefore, NO \cdot appears to be a very interesting reagent for the detection of nonconventional distonic ions. In contrast with the behaviour of cyanogen *N*-oxide ions, cyanogen *N*-sulfide and *N*-selenide radical cations readily react with NO \cdot by S $^{+}$ and Se $^{+}$ transfer, respectively. This different chemical behaviour of the NCCNX $^{+}$ ions (X = O, S, Se) in reacting with nitric oxide may be attributed to a strong double

bond character of the N–O linkage whereas, for X = S and X = Se, the N–X bond lengths are significantly longer [19]. Pyridine *N*-sulfide molecular ions, 1 $^{+}$, are *inter alia* differentiated from their conventional isomers because of the reactions with nitric oxide. Whereas the mercaptopyridine ions only react by charge exchange, SNO $^+$ cations are also produced when performing the reaction between 1 $^{+}$ and NO \cdot [3].

The ion–molecule reactions between 4 $^{+}$ or 5 $^{+}$ and nitric oxide have been performed in the quadrupole cell (Table 1). In addition to the charge exchange reaction, SeNO $^+$ cations (*m/z* 110) are generated in the reaction between 4 $^{+}$ and NO \cdot , but the yield of this Se $^{+}$ transfer is very low (less than 0.01% of the *m/z* 159 base peak). This reaction seems, nevertheless, very characteristic of the pyridine *N*-selenide structure because it is *not* observed in the case of the reference ions, 5 $^{+}$.

Se $^{+}$ transfers from 4 $^{+}$ to methyl isocyanide, CH $_3$ NC, or pyridine- d_5 leading, respectively, to ionized methyl isoselenocyanate, CH $_3$ NCSe $^{+}$ (*m/z* 121, 4% of the *m/z* 159 base peak) or ionized pyridine- d_5 *N*-selenide (*m/z* 164, 3% of the *m/z* 159 base peak) are more efficient reactions (Table 1). These reactions are again not observed in the case of the reference ions, 5 $^{+}$.



Scheme 3.

3.3. Ion–molecule reactions with dimethyl disulfide (DMDS) and dimethyl diselenide (DMDSe)

$\text{CH}_3\text{S}^\bullet$ abstraction from dimethyl disulfide, CH_3SSCH_3 , is a selective reaction for distonic ions. Whereas conventional radical cations (generated usually by removing one electron from a stable neutral molecule) undergo fast charge exchange with dimethyl disulfide, distonic radical cations are able to abstract $\text{CH}_3\text{S}^\bullet$ from DMDS (this reaction is often in competition with charge exchange). Hence, the observation of a $\text{CH}_3\text{S}^\bullet$ abstraction reaction is considered as a strong indication for the occurrence of a distonic structure [14c,20].

The pyridine *N*-selenide molecular ions, $4^{+\bullet}$, react with DMDS by charge exchange (m/z 94), Se^+ transfer to DMDS (m/z 174), and $\text{CH}_3\text{S}^\bullet$ abstraction from DMDS (m/z 206) [Scheme 3, Fig. 4(a)].

In order to gain more information on the structure of the ions produced in these ion–molecule reactions, their high energy (8 keV) CA spectra were recorded.

The CA spectrum [Fig. 4(b)] of the cations obtained by thiomethyl radical abstraction from DMDS (m/z 206) is characteristic of the proposed structure, 6^+ . Intense collision-induced fragments are, indeed, detected at m/z 191 ($-\text{CH}_3$), m/z 159 ($-\text{CH}_3\text{S}^\bullet$), m/z 127 (CH_3SSe^+ cations), and m/z 112 (SSe^+ cations). Isomeric ions 7^+ can be generated by $\text{CH}_3\text{Se}^\bullet$ abstraction from DMDS by pyridine *N*-sulfide radical cations, $1^{+\bullet}$ [3]. 6^+ and 7^+ cations are readily differentiated on the basis of a collision-induced dissociation: a signal at m/z 111 corresponding to pyridine *N*-sulfide radical cations, $1^{+\bullet}$ ($\text{CH}_3\text{Se}^\bullet$ loss) is the base peak of the CA spectrum of 7^+ cations [3]. This signal is not observed in the case of 6^+ ions [Fig. 4(b)].

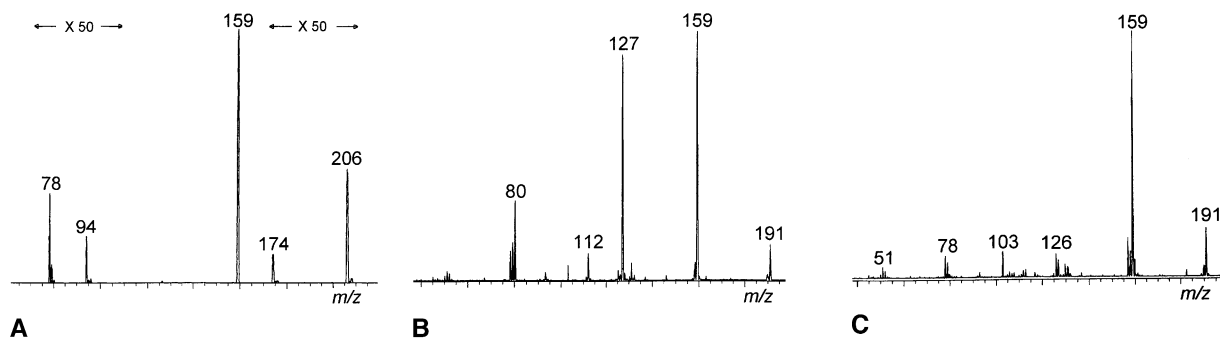
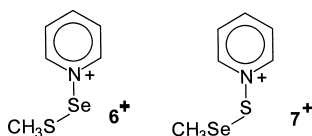


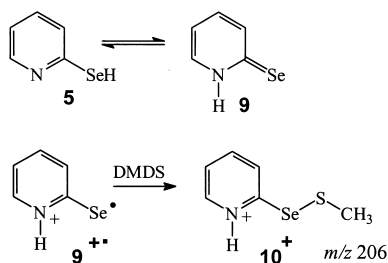
Fig. 4. Reaction between $4^{+\bullet}$ ions (m/z 159) and DMDS in the Qcell: (A) mass spectrum of the ion–molecule products, and (B) CA (O_2) spectrum of the $[4 + \text{CH}_3\text{S}]^+$ (m/z 206) cations. Reaction between $5^{+\bullet}$ ions and DMDS in the Qcell: (C) CA (O_2) spectrum of the $[5 + \text{CH}_3\text{S}]^+$ (m/z 206) cations.



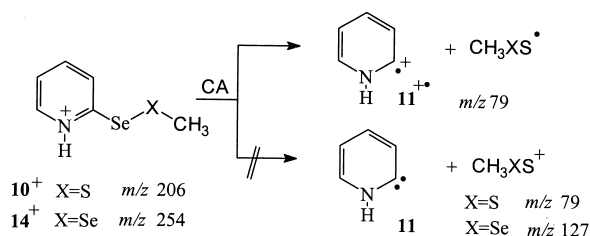
The high energy CA spectrum of the m/z 174 radical cations, resulting from the transfer of selenium ions to DMDS, is characterized by intense peaks at m/z 159 ($-CH_3$), m/z 126 ($-CH_3SH$), m/z 127 ($-CH_3S^\bullet$), m/z 128 ($-CH_2S$), and m/z 112 (SSe^{++}). These fragmentations can be ascribed to the dimethyl disulfide *S*-selenide connectivity, but direct insertion of Se^{++} into the labile S–S bond cannot be ruled out in the present experiment. Whatever the actual structure of these ions, the main results of this reaction are that (1) 4^{++} ions abstract CH_3S^\bullet from DMDS, and (2) Se^{++} is transferred from 4^{++} ions to neutral DMDS.

2-Selenopyridine molecular ions, 5^{++} , react also with DMDS by CH_3S^\bullet abstraction in addition to charge exchange (Table 1). This reaction was not unexpected because 2-selenopyridine, **5**, can exist in the gas phase as the tautomeric 2-pyridineselenone structure, **9** (Scheme 4). To the best of our knowledge, no experimental or theoretical evidence has appeared in the literature for the existence of this tautomeric structure. However, the analogous 2-hydroxypyridine and 2-mercaptopyridine were proved to coexist with their tautomeric isomers in the gas phase [21].

It is not unexpected that, in the molecular ions of **9**, the positive charge is localized on the nitrogen atom whereas the radical site is selenium. Such a resonance structure, 9^{++} , is therefore distonic and could consequently rationalize the CH_3S^\bullet abstraction (Scheme 4). A similar behaviour has been noticed previously for



Scheme 4.



Scheme 5.

the sulfur analogues of **4** and **5** [3]. Because ionized thioanisole was found unreactive in our experimental conditions, direct CH_3S^\bullet radical trapping by the thiol (selenol) tautomer followed by a 1,3-hydrogen shift appears unlikely. The CA spectrum of the 10^{++} cations [Fig. 4(c)] shows a very strong decrease in the intensity of the m/z 127 peak (CH_3SSe^{++} cations). The interpretation of the contrasting behaviour of 6^{++} and 10^{++} is straightforward. Indeed, Lavorato and co-workers have very recently calculated that neutral azacyclohexadiene-2-ylidene, **11**, is 50 kcal mol⁻¹ less stable than neutral pyridine [22]. In contrast, the relative stability of the corresponding radical cations has been found to be inverse, with the cyclic carbene ions, 11^{++} , being more stable than the conventional pyridine molecular ions. It is thus not surprising that the process leading to the generation of CH_3SSe^{++} cations plus the neutral carbene **11** in the fragmentation of 10^{++} is thermodynamically disfavoured (Scheme 5).

It is also noteworthy that Se^{++} transfer is not observed in the reaction of 5^{++} ions with DMDS. This clearly indicates that Se^{++} transfer from cyanogen *N*-selenide radical cations, 2^{++} , to neutral pyridine in the CI source or in the quadrupole collision cell leads specifically to pyridine *N*-selenide radical cations, 4^{++} , without any significant contribution of insertion in CH bonds.

Dimethyl diselenide (DMDS_{Se}) has been demonstrated as one of the most powerful reagents for the identification of distonic radical cations that often readily abstract CH_3Se^\bullet from DMDS_{Se} [23]. Unfortunately, the complexity of the isotopic distribution of selenium reduces the ion current and makes the spectra less easy to analyse.

Pyridine *N*-selenide molecular ions, 4^{+} , react with $\text{CH}_3\text{SeSeCH}_3$ by $\text{CH}_3\text{Se}^{\cdot}$ abstraction and Se^{+} transfer (Table 1) in addition to electron transfer, as depicted in Scheme 3. As expected, the molecular ions of 2-selenopyridine, 5^{+} , also react by charge exchange and by $\text{CH}_3\text{Se}^{\cdot}$ abstraction in the Qcell (Table 1), confirming the distonic character of the ionized tautomeric structure of selenopyridine. Again, ionized selenium transfer to DMDSe occurs for 4^{+} , not for 5^{+} .

4. Conclusions

A combination of high energy collisional activation and associative ion–molecule reaction experiments carried out in a single hybrid mass spectrometer of sectors–quadrupole–sectors configuration has allowed the characterization of a new distonic ion: the molecular ion of pyridine *N*-selenide. These ions are readily generated in the chemical ionization source or the quadrupole collision cell by reaction between NCCNSe^{+} ions and neutral pyridine. The interpretation of the NR results is less straightforward and does not unambiguously confirm the stability of the neutral dipole in the gas phase.

Acknowledgements

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References

- [1] A.R. Katritzky, J.M. Lagowski, *Chemistry of the Heterocyclic N-Oxides*, Academic, London, 1971.
- [2] (a) C. Wentrup, S. Fisher, A. Maquestiau, R. Flammang, *J. Org. Chem.* 51 (1986) 1908; (b) C. Wentrup, P. Kambouris, *Chem. Rev.* 91 (1991) 363.
- [3] P. Gerbaux, Y. Van Haverbeke, R. Flammang, *J. Mass Spectrom.* 32 (1997) 1170.
- [4] P. Gerbaux, Y. Van Haverbeke, R. Flammang, M.W. Wong, C. Wentrup, *J. Phys. Chem. A* 101 (1997) 6970.
- [5] R. Flammang, Y. Van Haverbeke, C. Braybrook, J. Brown, *Rapid Commun. Mass Spectrom.* 9 (1995) 795.
- [6] For reviews, see the following: (a) C. Wesdemiotis, F.W. McLafferty, *Chem. Rev.* 87 (1987) 485; (b) J.K. Terlouw, H. Schwarz, *Angew. Chem. Int. Ed. Engl.* 26 (1987) 805; (c) J.L. Holmes, *Mass Spectrom. Rev.* 8 (1989) 513; (d) F.W. McLafferty, *Science* 247 (1990) 925; (e) M. Plisnier, R. Flammang, *Chim. Nouv.* 8 (1990) 893; (f) N. Goldberg, H. Schwarz, *Acc. Chem. Res.* 27 (1994) 347; (g) C.A. Schalley, G. Hornung, D. Schröder, H. Schwarz, *Chem. Soc. Rev.* 27 (1998) 91.
- [7] P. Gerbaux, R. Flammang, E.H. Mørkved, M.W. Wong, C. Wentrup, *Tetrahedron Lett.* 39 (1998) 533.
- [8] P. Gerbaux, R. Flammang, E.H. Mørkved, M.W. Wong, C. Wentrup, *J. Phys. Chem. A* 102 (1998) 9021.
- [9] R.H. Bateman, J. Brown, M. Lefevre, R. Flammang, Y. Van Haverbeke, *Int. J. Mass Spectrom. Ion Processes* 115 (1992) 205.
- [10] Y. Cheng, T.J. Emge, J.G. Brennan, *Inorg. Chem.* 33 (1994) 3711.
- [11] R.E. Schuster, J.E. Scott, J. Casanova Jr., *Org. Synth.* 46 (1966) 75.
- [12] (a) C.G. De Koster, J.J. Van Houte, J. Van Thuijl, *Int. J. Mass Spectrom. Ion Processes* 98 (1990) 235; (b) S.J. Yu, M.L. Gross, K.R. Fountain, *J. Am. Soc. Mass Spectrom.* 4 (1993) 117; (c) F.C. Gozzo, M.N. Eberlin, *J. Am. Soc. Mass Spectrom.* 6 (1995) 554; (d) W.J. Bouma, J.K. MacLeod, L. Radom, *Adv. Mass Spectrom.* 8a (1980) 178; (e) M.W. van Amsterdam, H.W. Zappey, S. Ingemann, N.M.M. Nibbering, *Org. Mass Spectrom.* 22 (1987) 770; (f) C.G. de Koster, J.J. van Houte, J.B. Shadid, J. van Thuijl, *Rapid Commun. Mass Spectrom.* 2 (1988) 97; (g) C. Lange, *Org. Mass Spectrom.* 28 (1997) 1285.
- [13] (a) K. Levsen, H. Schwarz, *Mass Spectrom. Rev.* 2 (1983) 77; (b) J.L. Holmes, *Org. Mass Spectrom.* 20 (1985) 169.
- [14] (a) B.J. Shay, M.N. Eberlin, R.G. Cooks, C. Wesdemiotis, *J. Am. Soc. Mass Spectrom.* 3 (1992) 518; (b) K.M. Stirk, L.K.M. Kiminkinen, H.I. Kenttämaa, *Chem. Rev.* 92 (1992) 1649; (c) P. Gerbaux, R. Flammang, M.T. Nguyen, J.-Y. Salpin, G. Bouchoux, *J. Phys. Chem. A* 102 (1998) 861; (d) M.N. Eberlin, N.H. Morgon, S.S. Yang, B.J. Shay, R.G. Cooks, *J. Am. Soc. Mass Spectrom.* 6 (1995) 1; (e) M.N. Eberlin, R.G. Cooks, *J. Am. Chem. Soc.* 115 (1993) 9226.
- [15] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, *J. Phys. Chem. Ref. Data* 17 (1988) (suppl.).
- [16] (a) K.M. Stirk, R.B. Smith, J.C. Orlowski, H.I. Kenttämaa, *Rapid Commun. Mass Spectrom.* 7 (1993) 392; (b) D. Wittneben, H.-F. Grützmaier, *Int. J. Mass Spectrom. Ion Processes* 100 (1990) 545.
- [17] W.J. Bouma, J.K. MacLeod, L. Radom, *J. Chem. Soc. Chem. Commun.* (1978) 724.
- [18] T. Weiske, H. van der wel, N.M.M. Nibbering, H. Schwarz, *Angew. Chem. Int. Ed. Engl.* 23 (1984) 733.
- [19] R. Flammang, M. Barbioux-Flammang, P. Gerbaux, C. Wentrup, M.W. Wong, *Bull. Soc. Chim. Belg.* 106 (1997) 545.
- [20] K.M. Stirk, J.C. Orlowski, D.T. Leeck, H.I. Kenttämaa, *J. Am. Chem. Soc.* 114 (1992) 8604.

- [21] (a) P. Beak, F.S. Fry Jr., J. Lee, F. Steele, *J. Am. Chem. Soc.* 98 (1976) 171; (b) A. Maquestiau, Y. Van Haverbeke, R. Flammang, H. Mispreuve, A.R. Katritzky, J. Ellison, J. Frank, Z. Meszaros, *Bull. Soc. Chim. Belg.* 88 (1979) 395; (c) A. Maquestiau, Y. Van Haverbeke, C. De Meyer, A.R. Katritzky, J. Frank, *Bull. Soc. Chim. Belg.* 84 (1975) 465; (d) R.A.J. O'Hair, M.A. Freitas, J.A.R. Schmidt, M.E. Hatley, *Eur. Mass Spectrom.* 1 (1995) 457; (e) P.B. Terent'ev, A.G. Kalandarishvili, *Mass Spectrom. Rev.* 15 (1997) 339.
- [22] D. Lavorato, J.K. Terlouw, T.K. Dargel, W. Koch, G.A. McGibbon, H. Schwarz, *J. Am. Chem. Soc.* 117 (1996) 1189.
- [23] (a) B.J. Beasley, R.L. Smith, H.I. Kenttämää, *J. Mass Spectrom.* 30 (1995) 384; (b) K.K. Thoen, B.J. Beasley, R.L. Smith, H.I. Kenttämää, *J. Am. Soc. Mass Spectrom.* 7 (1996) 1245.