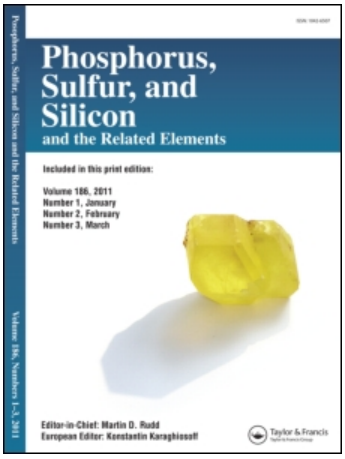

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THE INTRIGUING DIVERSITY OF NEUTRAL AND CATIONIC SELENIUM-NITROGEN HETEROCYCLES

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Abstract Salts containing ternary Se,N,Cl cations, $[(SeCl)_2N]^+X^-$ ($X^- = SbCl_6^-$, **1**; $FeCl_4^-$, **2**) and $[(SeCl_2)_2N]^+Y^-$ ($Y^- = AsF_6^-$, **3**), were prepared by reaction of $N(SiMe_3)_3$ with $[SeCl_3]^+X^-$ or $[SeCl_3]^+Y^-$, respectively. In addition, **1** was formed from the reaction of Se_2NCl_3 with $SbCl_5$. The structures of **1** - **3** were determined by X-ray crystallography. Reaction of **1** with $F_3C\text{-}C{\equiv}C\text{-}CF_3$ led to the formation of the novel five-membered heterocyclic cation $[F_3C\text{-}\overbrace{C\text{-}Se\text{-}N\text{-}Se\text{-}C}\text{-}CF_3]^+$ ($[SbCl_6]^-$ salt, **4**). Compound **4** turned out to be a useful building block to generate new selenium containing heterocycles such as the neutral rings $F_3C\text{-}\overbrace{C\text{-}Se\text{-}N\text{-}Se\text{-}C}\text{-}CF_3$ (7π radical) (**5**), $F_3C\text{-}\overbrace{C\text{-}Se\text{-}Se\text{-}C}\text{-}CF_3$ (**6**) and $F_3C\text{-}\overbrace{C\text{-}Se\text{-}Se\text{-}C(CF_3)\text{-}C(CF_3)\text{-}Se\text{-}Se\text{-}C}\text{-}CF_3$ (**7**). The heterocycle **6** was shown by electron diffraction studies to have a close to planar four-ring structure. The solid state structure of compound **7** was determined by X-ray crystallography. The existence of the neutral radical **5** was established by means of neutralization-reionization mass spectrometry. The structures of **6** and of the cation in **4** were computed ab initio using model compounds in which the CF_3 groups were replaced by a fluorine atom (i.e. $F\text{-}\overbrace{C\text{-}Se\text{-}Se\text{-}C}\text{-}F$ for **6** and $[F\text{-}\overbrace{C\text{-}Se\text{-}N\text{-}Se\text{-}C}\text{-}F]^+$ for the cation in **4**.

RESULTS AND DISCUSSION

During the last few years, significant advances have been made in the area of Se-N chemistry.[1-3] The objective of these studies has always been the preparation of polymeric $(SeN)_x$ which may exhibit more unusual properties than the superconductor $(SN)_x$. Several Se-N chlorides that are potential building blocks, because they are sources of the

SeNSe unit have been synthesized for the first time recently. The first examples of ternary Se,N,Cl cations were the cations $[N(SeCl_2)_2]^+$ and $[N(SeCl)_2]^+$. The former one was prepared by reaction of $[SeCl_3]^+[AsF_6]^-$ with $N(SiMe_3)_3$ [equation (1)].[4]

$$6\ [SeCl_3]^+[AsF_6]^- + 5\ N(SiMe_3)_3 \longrightarrow 9\ Me_3SiF + 3\ AsF_3 + N_2 + 6\ Me_3SiCl + 3\ [N(SeCl_2)_2]^+[AsF_6]^- \quad (1)$$

The $[N(SeCl)_2^+]$ cation was prepared on different reaction pathways as its $[GaCl_4]^-$, $[FeCl_4]^-$ or its $[SbCl_6]^-$ salt, respectively.[5-6] $[N(SeCl)_2]^+[GaCl_4]^-$ was obtained from the reaction of Se_2NCl_3 with the Lewis acid $GaCl_3$ [equation (2)] whereas $[N(SeCl)_2]^+[SbCl_6]^-$ was prepared by the reaction of $[SeCl_3]^+[SbCl_6]^-$ with $N(SiMe_3)_3$ [equation (3)].

$$Se_2NCl_3 + GaCl_3 \longrightarrow [N(SeCl)_2]^+[GaCl_4]^- \quad (2)$$

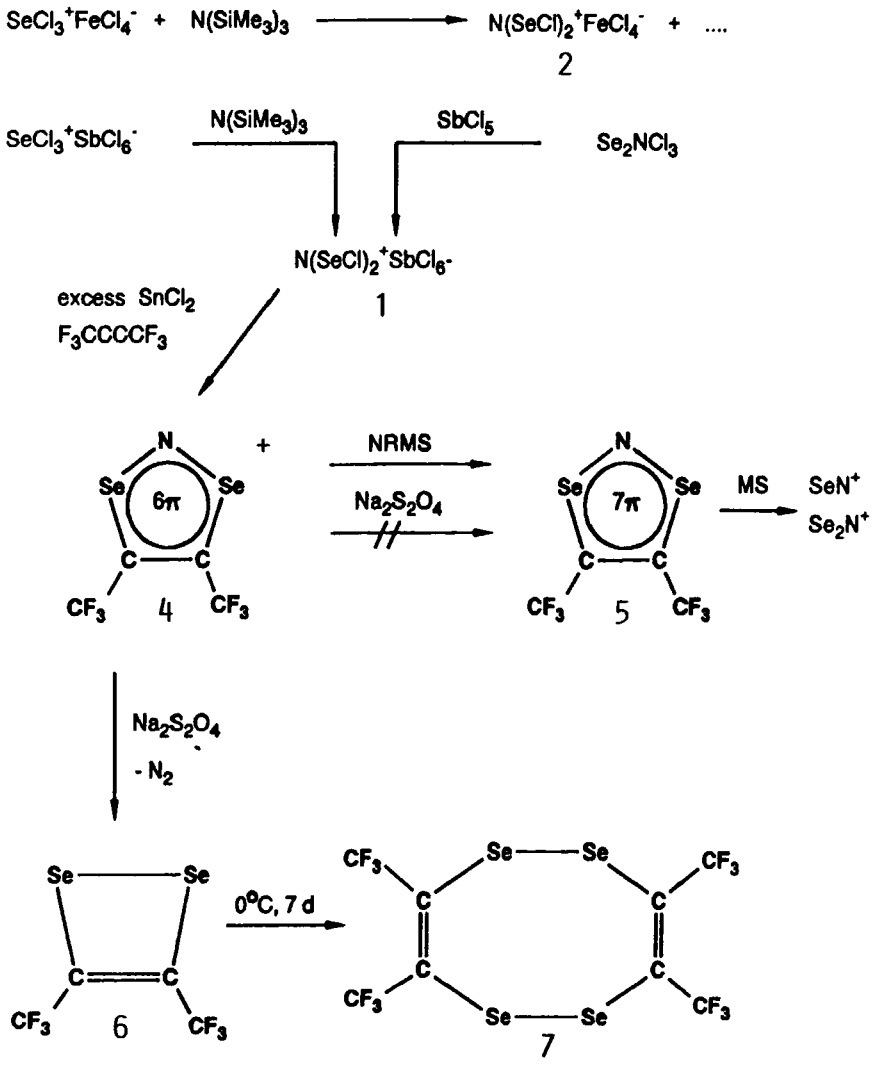
$$2\ [SeCl_3]^+[SbCl_6]^- + N(SiMe_3)_3 \longrightarrow [N(SeCl)_2]^+[SbCl_6]^- + SbCl_5 + Cl_2 + 3\ Me_3SiCl \quad (3)$$

The solid state structure of the cation $[N(SeCl)_2]^+$ depends on its counter anion. It exists in the crystalline state either as the u-isomer ($[GaCl_4]^-$, $[FeCl_4]^-$ salt) or as the s-isomer ($[SbCl_6]^-$ salt), because both isomers are essentially identical in their total energy (ΔE,MP2 = 1 kcal/mol), which was shown by ab initio computations.[6,7]

Not only is the $[N(SeCl)_2]^+$ cation of general interest in terms of structure and bonding, it is also as a very useful building block in preparative chemistry to synthesize heterocycles like $[F_3C\text{-}\overline{C\text{-}Se\text{-}N\text{-}Se\text{-}C}\text{-}CF_3]^+[SbCl_6]^-$ (**4**), $F_3C\text{-}\overline{C\text{-}Se\text{-}N\text{-}Se\text{-}C}\text{-}CF_3$ (**5**), $F_3C\overline{CSeSeC}CF_3$ (**6**) and $F_3C\text{-}\overline{C\text{-}Se\text{-}Se\text{-}C(CF_3)\text{-}C(CF_3)\text{-}Se\text{-}Se\text{-}C}\text{-}CF_3$ (**7**). The synthesis of **4** by reaction of **1** with $F_3CC{\equiv}CCF_3$ and $SnCl_2$ is very interesting, because the formation of the still unknown Se_2N^+ cation as an intermediate is more than likely. In this contribution we also report on ab initio MO calculations for $F\text{-}\overline{C\text{-}Se\text{-}N\text{-}Se\text{-}C}\text{-}F^+$ and $F\text{-}\overline{C\text{-}Se\text{-}Se\text{-}C}\text{-}F$. We also present the results of NRMS experiments of compound **4**. The most interesting feature of the NR mass spectrum of **4** corresponds to the peak of re-ionized neutral **5**, thus establishing the intrinsic stability of neutral $F_3C\text{-}\overline{C\text{-}Se\text{-}N\text{-}Se\text{-}C}\text{-}CF_3$ in the gas phase.

An overview of all experiments presented in this contribution is illustrated in SCHEME 1.

A full report on all experimental details of these structural and spectroscopic studies will be published shortly.[8]



SCHEME 1 Reaction scheme

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