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Is Se-Se bond cleavage the most favourable process in electron attachment to diselenides? The importance of asymmetry

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Supporting Information

(a total of 5 pages)

Computational Methods

Density Functional Theory (DFT) is frequently used for the theoretical modeling of peptides and proteins due to its high accurate results at low computational price. However, standard approximate functionals suffer from the self-interaction error (an unbalanced description of the Coulomb and exchange terms) which becomes especially important for odd-electron system[1-3], as is the case for the electron attachment processes investigated in this study. This problem has been renamed more recently as delocalization error[4], present when, due to delocalization, atomic centers bear fractional charges, what makes approximate functionals to underestimate the energy of such systems. Besides, DFT does not give a proper description of weak interactions with a high dispersive nature, as it is the case for some of the complexes present in this study. Consequently, MP2 perturbation theory has been preferred for geometry optimizations, able to recover enough electronic correlation at a computationally affordable cost for the systems here considered. For this purpose, the 6-31++G(d,p) (BS1) basis set has been chosen since it provides enough flexibility to describe the bonding situations we deal with. Diffuse functions are necessary to describe the extra electron placed far from the nuclei in the anions. The converged structures were identified as real minima of the potential energy surface by evaluation of the Hessian matrix. Although the basis set BS1 is flexible enough for geometry optimizations, final energies will be obtained with single-point calculations with a more extended basis set expansion, namely aug-cc-pVTZ (BS2), and the CCSD(T) method. Geometry optimizations and Hessian evaluations with BS1 have been performed with the Gaussian03 suite of programs[5], while the single point calculations with BS2 at CCSD(T) level were carried out with the MOLPRO 2009.01 package[6].

To rationalize some of the processes involved in the present paper several electronic states need to be analyzed. Moreover, some of the reactions occur through the crossing of different Potential Energy Surfaces (PES), what makes compulsory the use of multireference methods, among which the CASSCF/CASPT2 approach has been chosen. Geometries were optimized, when needed, at the CASSCF level with Atomic Natural Orbital (ANO) basis set described by Pierloot et al.[7] contracted to Se[5s4p3d]/C,N,O,F[3s2p1d]/H[2s1p] (BS3). With these geometries, high-level energies were obtained with the multireference second-order perturbation CASPT2 method and using the same BS2 as for the other methods. The active space was formed by distributing 10 electrons (11 in the case of anions) in 8 orbitals (9 for the anions), which showed good results in a similar study involving disulfides[8]. In situations where two states were close at the CASPT2 level, the Multistate CASPT2 (MS-CASPT2) method was employed to check that the level crossings were not an artifact of the non-orthogonality of the CASPT2 solutions[9]. The multireference calculations were performed with the MOLCAS 7.2 package of programs[10].

Structure of the Compounds of This Study

Figure S1 contains the main geometrical parameters of the neutral and anionic $CH_3SeSeCH_3$, $CH_3SeSeNH_2$ and CH_3SeSeF molecules. The full structure of these derivatives can be obtained by the Cartesian coordinates contained in Table S1. As commented in the Computational Details, the structures were calculated at the MP2 level with the 6-31+G(d,p) basis set expansion.

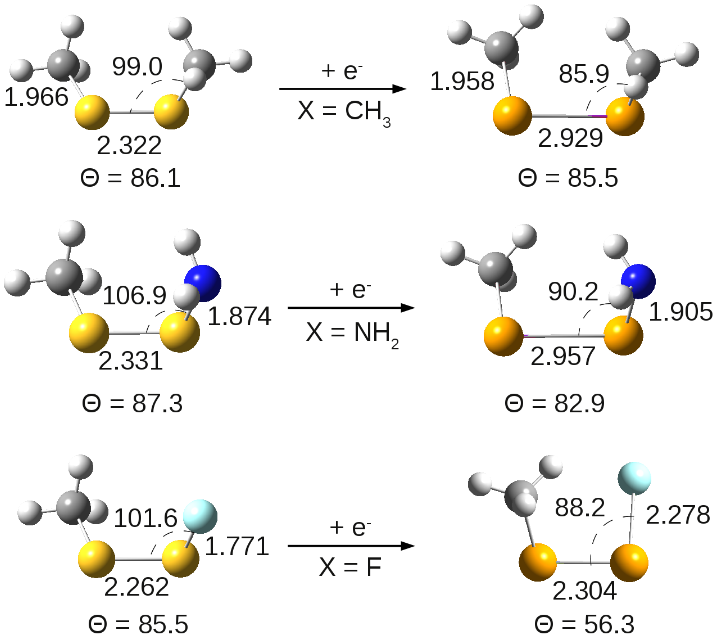

Figure S1. Main bond lengths (in Å) and angles (in °) for the neutral and anionic $CH_3SeSeCH_3$, $CH_3SeSeNH_2$ and CH_3SeSeF molecules. The dihedral angle (Θ) corresponds to that formed among the CSeSeX atoms.

Table S1 Cartesian Coordinates (in Ångstroms) of the optimized geometries at the MP2/631++G(d,p) level of the neutral and anionic CH3SeSeX (X = CH3, NH2, F) series of molecules.

$CH_3SeSeCH_3$

	Neutral			Anion		
Se	-0.6500	0.6967	-1.2165	-0.6097	0.9297	-1.4429
Se	-0.1177	-0.7808	0.4933	-0.1490	-0.9546	0.7515
C	1.2728	-1.8160	-0.4176	1.1742	-1.7950	-0.4357
H	2.0846	-1.1558	-0.7242	1.9633	-1.0796	-0.6759
H	1.6418	-2.5491	0.3052	1.6098	-2.6665	0.0643
H	0.8565	-2.3344	-1.2824	0.7001	-2.1188	-1.3662
C	-1.9694	-0.3953	-2.1659	-1.8722	-0.4078	-2.1386
H	-2.7950	-0.6422	-1.4979	-2.6768	-0.5674	-1.4179
H	-2.3341	0.2095	-3.0010	-2.2934	-0.0527	-3.0850
H	-1.5054	-1.3048	-2.5500	-1.3625	-1.3597	-2.3108

$CH_3SeSeNH_2$

	Neutral			Anion		
Se	1.2303	0.9823	1.1762	1.3747	1.1070	1.3577
Se	-0.0541	-0.8667	0.5729	-0.3644	-1.1064	0.4536
C	0.9780	2.0876	-0.4219	1.0217	1.9406	-0.3869
H	-0.0845	2.2748	-0.5795	-0.0361	2.1773	-0.4817
H	1.4981	3.0320	-0.2401	1.6055	2.8570	-0.4800
H	1.4112	1.5963	-1.2943	1.3008	1.2670	-1.1970
N	1.0505	-2.0009	-0.3782	1.1007	-1.8867	-0.4805
H	1.3943	-1.5723	-1.2367	1.3904	-1.2160	-1.1887
H	1.8359	-2.3234	0.1865	1.8664	-1.9303	0.1885

CH_3SeSeF						
	Neutral			Anion		
Se	-0.5682	0.6420	-1.2523	-0.1081	-0.0282	-0.0861
Se	-0.0482	-0.6818	0.5071	-0.0150	0.0389	2.2253
C	-1.9232	-0.4670	-2.1312	1.8265	-0.0078	-0.3779
H	-2.7631	-0.6131	-1.4589	2.2497	-0.9610	-0.0655
H	-2.2429	0.0694	-3.0232	2.0178	0.1658	-1.4381
H	-1.4774	-1.4179	-2.4069	2.2093	0.8057	0.2360
F	1.2072	-1.7619	-0.2056	1.2116	1.9410	2.0512

Energy Profiles of the Electron Capture Dissociations of $CH_3SeSeNH_2$

Fig. S1 represents the energy profiles of the possible fragmentations of $CH_3SeSeNH_2$ triggered by electron attachment. Although it is a bit more complex than that of the corresponding CH3SeSeCH3 system (Fig. 3 of the Main Paper) due to the more products available, both PES essentially represent the same picture: the release of neutrals (CH_4 and NH_3) is more favorable from a thermodynamic perspective but it involves high energy barriers.

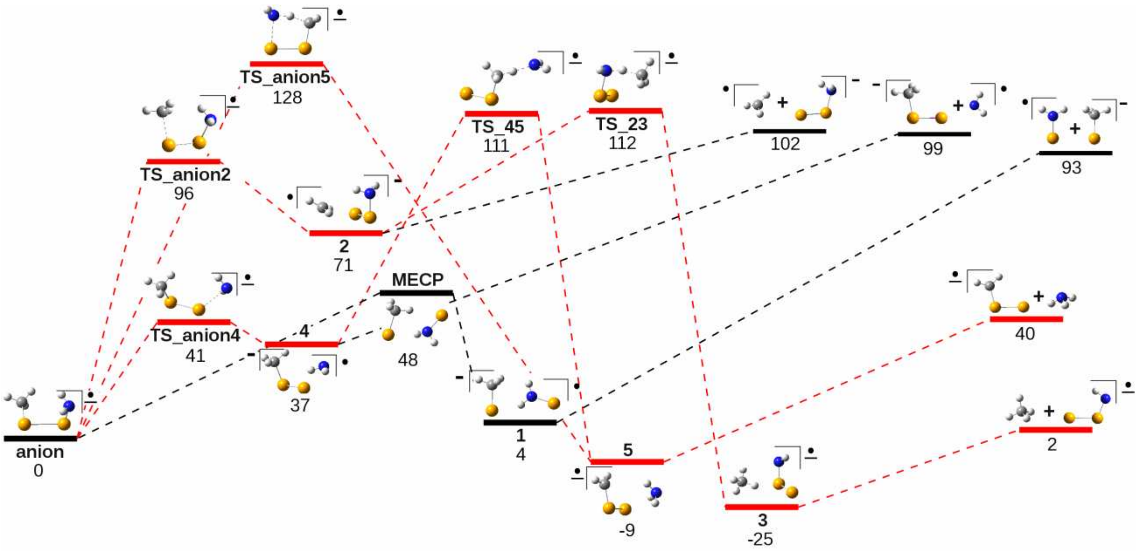

Figure S1 Energy profile associated with the main fragmentations of $[CH_3SeSeNH_2]^-$. The paths leading to the loss of CH_4 and NH_3 are highlighted in red. Relative ΔH values (in kJ mol^{-1}) calculated at the CCSD(T)/aug-cc-pVTZ level are displayed under each structure. For the MECP structure, the CASPT2 method was used instead.

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