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Experimental and Theoretical Investigations of Structural Trends for Selenium(IV) Imides and Oxides: X-ray Structure of $Se_3(NAd)_2$

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The thermal decomposition of $Se(NAd)_2$ (Ad = 1-adamantyl) in THF was monitored by ^{77}Se NMR and shown to give the novel cyclic selenium imide $Se_3(NAd)_2$ as one of the products. An X-ray structural determination showed that $Se_3(NAd)_2$ is a puckered five-membered ring with $d(Se–Se) = 2.404(1)$ Å and $|d(Se–N)| = 1.873(4)$ Å. On the basis of ^{77}Se NMR data, other decomposition products include the six-membered ring $Se_3(NAd)_3$, and the four-membered rings $AdNSe(\mu\text{-}NAd)_2SeO$ and $OSe(\mu\text{-}NAd)_2SeO$. The energies for the cyclodimerization of $E(NR)_2$ and RNEO (E = S, Se; R = H, Me, ^tBu, $SiMe_3$), and the cycloaddition reactions of RNSeO with $E(NR)_2$, $RNSO_2$ with $Se(NR)_2$, and $S(NR)_2$ with $Se(NR)_2$ have been calculated at MP2, CCSD, and CCSD(T) levels of theory using the cc-pVDZ basis sets and B3PW91/6-31G* optimized geometries. Sulfur(IV) and selenium(IV) diimide monomers are predicted to be stable, the sole exception being $Se(NSiMe_3)_2$ that shows a tendency toward cyclodimerization. The cyclodimerization energy for RNSeO and the cycloaddition reaction energies of RNSeO with $Se(NR)_2$ as well as that of $RNSO_2$ with $Se(NR)_2$ are negative, consistent with the observed formation of $OSe(\mu\text{-}N^tBu)_2SeO$, $OSe(\mu\text{-}N^tBu)_2SeN^tBu$, and $O_2S(\mu\text{-}N^tBu)_2SeN^tBu$, respectively. Cycloaddition is unlikely when one of the reactants is a sulfur(IV) diimide.

Introduction

The chemistry of imido derivatives of selenium in various oxidation states has developed slowly compared to the extensively studied acyclic[1] and cyclic[2,3] sulfur−imide systems. The first selenium(IV) diimide $Se(N^tBu)_2$ (**1a**) was reported by Sharpless et al. more than 25 years ago.[4] These reactive species are efficient in situ reagents for allylic amination of olefins and 1,2-diamination of 1,3-dienes.[4,5] The selenium(IV) diimide **1a** forms an *N,N′*-chelated adduct with $SnCl_4$.[6] It has also been used to generate the pyramidal dianion $[Se(N^tBu)_3]^{2-}$, isoelectronic with SeO_3^{2-}, by reaction with 2 equiv of $LiNH^tBu$.[7] Multinuclear NMR studies of **1a** by Wrackmeyer et al. indicated a monomeric structure with a *syn,anti* configuration in solution.[8] Monomeric structures are also found exclusively for sulfur(IV) diimides.[1] By contrast, the corresponding tellurium(IV) imide, $^tBuNTe(\mu\text{-}N^tBu)_2TeN^tBu$, is dimeric in solution and in the solid state.[9] Consistently, density functional calculations on the model systems $E(NMe)_2$ (E = S, Se, Te) predict that the dimerization is highly exothermic for E = Te and endothermic for E = S, in agreement with experimental observations, but approximately thermoneutral for E = Se.[10]

In a preliminary communication, we showed by X-ray crystallography that $Se(NAd)_2$ (**1b**, Ad = 1-adamantyl) is a

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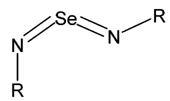
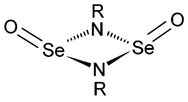
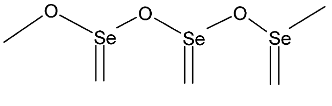
syn,*anti*-monomer in the solid state,[11] in agreement with the conclusions of solution NMR studies of **1a**.[8] Interestingly, the hybrid imido−oxo system (seleninylamine) OSe(μ-N^{t}Bu)$_2$SeO (**2a**), first reported by Herberhold in 1986,[12] forms a dimer with the oxo ligands in a *cis* configuration in the solid state.[11] The third member of this isoelectronic series, (SeO$_2$)$_\infty$ (**3**), has a polymeric chain structure.[13] The unsymmetrical imido−oxo species ^{t}BuNSe(μ-N^{t}Bu)$_2$SeO (**4a**) has a cyclic structure similar to that of **2a**.[14]



1a, R = ^{t}Bu
1b, R = Ad



2a, R = ^{t}Bu
2b, R = Ad



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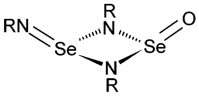
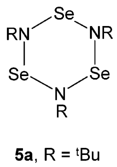
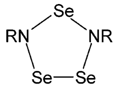


4a, R = ^{t}Bu
4b, R = Ad

The limited information available on cyclic selenium imides indicates the existence of a more varied series of macrocycles compared to their sulfur analogues, which are primarily limited to eight-membered rings S$_{8-x}$(NH)$_x$ (x = 1−4) that are structurally related to cyclooctasulfur.[2,3] Early work by Roesky et al. led to the structural characterization of the eight-membered ring Se$_6$(N^{t}Bu)$_2$ and the 15-membered ring Se$_9$(N^{t}Bu)$_6$.[15] More recently, we have shown that the six-membered ring Se$_3$(N^{t}Bu)$_3$ (**5a**) is formed, in addition to the acyclic imidoselenium(II) dihalides ClSe[N(^{t}Bu)Se]$_n$Cl (n = 1,2), from the reaction of SeCl$_2$ with *tert*-butylamine in THF.[16] The tellurium analogue Te$_3$(N^{t}Bu)$_3$ is also known.[9] Subsequently, it was shown that **5a** and Se$_9$(N^{t}Bu)$_6$ are the major products of the thermal decomposition of **1a**.[14] A third product of this decomposition was identified, on the basis of analytical and spectroscopic data, as a member of the homologous series [Se$_3$(N^{t}Bu)$_2$]$_n$ (n = 1 or 2).[14]



5a, R = ^{t}Bu
5b, R = Ad



6a, R = ^{t}Bu
6b, R = Ad

We have now investigated by ^{77}Se NMR the thermal decomposition of **1b** which leads to the novel five-membered ring **6b**, in addition to the six-membered ring **5b** and the partial hydrolysis products **2b** and **4b**. In order to rationalize the structures of the imidoselenium(IV) systems **1**, **2**, and **4**, we have also carried out high level quantum chemical calculations of the energetics for the cyclodimerization of E(NR)$_2$ and RNEO (E = S, Se; R = H, Me, ^{t}Bu, SiMe$_3$), and some related cycloaddition reactions.

Experimental Section

General Considerations. All manipulations involving air-sensitive materials were conducted under an argon atmosphere by using Schlenk techniques or in a drybox. Solvents were dried and distilled under an argon atmosphere prior to use: tetrahydrofuran and diethyl ether (LiAlH$_4$) and *n*-hexane (Na/benzophenone). ^{t}BuNH$_2$ (Aldrich) was distilled over KOH and stored over molecular sieves. Selenium powder, SeCl$_4$, and SO$_2$Cl$_2$, and 1-adamantylamine (AdNH$_2$) (Aldrich) were used without further purification. Se(NAd)$_2$ was prepared by the reaction of AdNH$_2$ with SeCl$_4$ in THF as previously described.[11] ^{t}BuNSeO was obtained from OSeCl$_2$ with ^{t}BuNH$_2$ by the literature procedure.[12]

Instrumentation. ^{1}H NMR spectra were recorded on a Bruker AC-200 or a Bruker AM-400 spectrometer. The ^{13}C, ^{14}N, and ^{77}Se NMR spectra were recorded on a Bruker AM-400 or a Bruker DPX-400 spectrometer operating at 100.614, 28.915, and 76.312 MHz, respectively. The spectral widths were 23.81, 29.41, and 100.00 kHz, yielding the respective resolutions of 1.45, 3.59, and 6.10 Hz/data point. The ^{13}C pulse width was 3.50 μs, for ^{14}N 20.0 μs, and for ^{77}Se 9.00 μs. The ^{13}C, ^{14}N, and ^{77}Se accumulations contained 1000−20 000, 20 000−200 000, and 15 000−30 000 transients, respectively. Relaxation delays used were ^{13}C 3.0 s, ^{14}N 1 ms, and ^{77}Se 2 s. The ^{14}N NMR spectra are reported relative to neat CH$_3$NO$_2$. All ^{77}Se NMR spectra were referenced externally to a saturated solution of SeO$_2$ in D$_2$O at room temperature. The chemical shifts are reported relative to neat Me$_2$Se at room temperature [δ(Me$_2$Se) = δ(SeO$_2$) + 1302.6].

Preparation of Se$_3$(NAd)$_2$ (6b). A white slurry of 1-adamantylamine (2.055 g, 13.59 mmol) in diethyl ether (10 mL) was added to a pale yellow slurry of SeCl$_4$ (0.500 g, 2.265 mmol) in diethyl ether (15 mL) at −38 °C. The reaction mixture was allowed to reach ca. 23 °C, and after 4 h, a pale yellow precipitate was removed by filtration through a sintered glass filter disk (8 μm) and PTFE syringe filter (0.45 μm). The precipitate was shown to be primarily [AdNH$_3$]Cl (2.243 g) by ^{1}H NMR. Removal of solvent from the yellow filtrate under vacuum gave a yellow solid (0.153 g, 0.286 mmol, 38% based on Se), which contained no [AdNH$_3$]Cl (^{1}H and ^{13}C NMR, IR). Yellow-orange needles of Se$_3$(NAd)$_2$ were obtained from a C$_7$D$_8$ solution of this product in an NMR tube. Anal. Calcd for C$_{20}$H$_{30}$N$_2$Se$_3$: C, 44.87; H, 5.65; N, 5.23. Found: C, 45.81; H, 5.78; N, 5.33. NMR: δ ^{77}Se (C$_7$D$_8$, 25 °C) 1380 and 1083 (relative intensities 1:2).

X-ray Analysis. Diffraction data for **6b** were collected on a Nonius KappaCCD 4-Circle Kappa FR540C diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Crystallographic data are given in Table 1. The intensity data were corrected for Lorentz and polarization effects, and for absorption (SADABS).[17]

A yellow needlelike crystal of **6b** (0.15 × 0.08 × 0.03 mm^3) was coated with Paratone oil and mounted in a nylon CryoLoop. The structure was solved by using direct methods with SHELXS-

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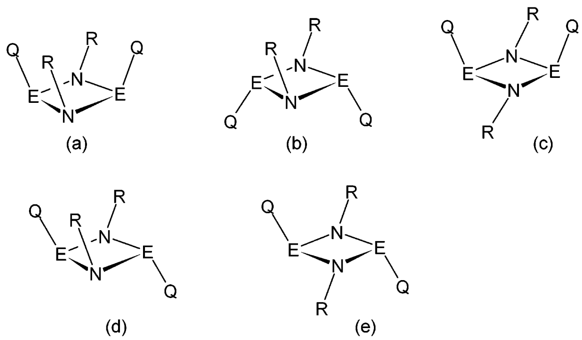
Table 1. Crystallographic Data for $Se_3(NAd)_2$ (**6b**)

formula	$C_{20}H_{30}N_2Se_3$
fw	535.34
cryst syst	monoclinic
space group	$C2/c$ (No. 15)
a, Å	27.2590(2)
b, Å	6.5850(4)
c, Å	21.6340(9)
α, deg	90
β, deg	100.152(1)
γ, deg	90
V	3822.5(3)
Z	8
T, K	173
ρ_{calcd}, g cm^{-3}	1.860
μ(Mo Kα), cm^{-1}	75.80
R1[a]	0.0543
wR2[b]	0.0784

[a] $R1 = [\Sigma||F_o| - |F_c||]/[\Sigma|F_o|]$ $[I \geq 2\sigma(I)]$. [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$ [all data].

Chart 1. Conformations of the Relevant Cycloaddition and Dimerization Products [E = S, Se; Q = NR, O_x (x = 1, 2); R = H, Me, ^{t}Bu, $SiMe_3$]



97[18] and refined by full-matrix least-squares methods on F^2 with SHELXL97-2.[19] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions (C−H = 0.95 Å) and were not refined.

Computational Details

All calculations were carried out with Gaussian 98[20] and Molpro[21] sets of programs. Geometries of all molecules were fully optimized at the B3PW91[22,23] level of theory using standard Pople-type 6-31G* basis set as implemented in Gaussian 98.[24] All relevant conformers based on the [2 + 2] cycloaddition reaction were considered in the calculations (see Chart 1). The fundamental frequencies were also calculated in order to assess the nature of the stationary points and to estimate the zero-point correction to the energy (ZPE).

Three different higher-level theoretical methods were employed in the computation of energetics. Single point calculations at all B3PW81/6-31G* optimized geometries were carried out with the MP2,[26] CCSD, and CCSD(T) methods.[27] However, coupled cluster calculations required excessive computational resources for ^{t}Bu or $SiMe_3$ derivatives and were not carried out. Therefore, single point MP2 calculations utilizing B3PW91/6-31G* optimized geometries provide the most accurate energies that could be computed for all molecular systems reported in this work. Dunning's correlation consistent basis set of double-ζ quality, cc-pVDZ were used in all single point calculations.[28] In case of small molecular systems $E(NH)_2$ and $HNEO_x$ (E = S, Se, x = 1,2) and their cyclodimerization and cycloaddition products, the calculations were repeated by using the triple-ζ quality cc-pVTZ basis.[28]

Results and Discussion

^{77}Se NMR Study of the Decomposition of $Se(NAd)_2$ (1b). We have previously monitored the decomposition of **1a** over a period of 8 days by ^{77}Se NMR.[14] The major products are the six-membered ring **5a**, the heterocycle $[Se_3(N^tBu)_2]_n$ (n = 1 or 2), which was not structurally characterized, and the 15-membered ring $Se_9(N^tBu)_6$. In order to obtain further insights into the formation of cyclic selenium imides from acyclic selenium(IV) diimides, we have now investigated the thermal decomposition of the new derivative **1b**[11] by ^{77}Se NMR.

The ^{77}Se NMR spectrum of the THF solution of **1b** that is recorded immediately after the preparation exhibits only one major resonance at 1662.4 ppm. Within 1 day, several minor resonances have appeared, and their relative intensities with respect to that of **1b** continue to grow with time. The ^{77}Se NMR spectrum of the solution after 3 days is shown in Figure 1 together with the assignments of the resonances, based on the identification of the decomposition products of $Se(N^tBu)_2$.

The major resonance at 1361 ppm is attributed to the six-membered ring $Se_3(NAd)_3$ (**5b**). The *tert*-butyl derivative **5a** exhibits a ^{77}Se resonance at 1396 ppm.[16] The two resonances at 1380 and 1083 ppm (approximate intensity ratio 1:2) are assigned to the five-membered ring $Se_3(NAd)_2$ (**6b**), cf. 705

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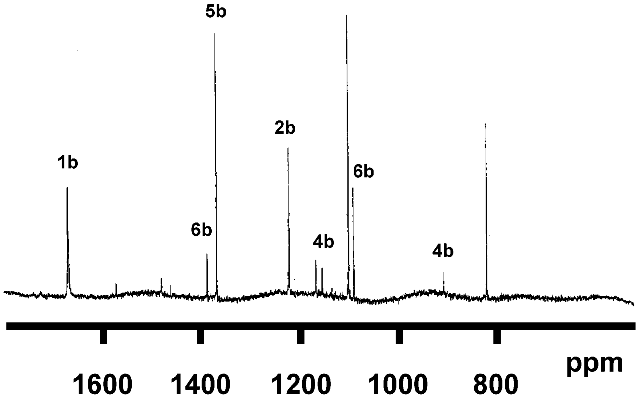

Figure 1. The ^{77}Se NMR spectrum of the decomposition mixture of AdN=Se=NAd (**1b**) in THF at 25 °C after 3 days.

and 522 ppm for the related ring system $Se_3(AsPh)_2$.[29] The substantial downfield shift of these resonances in **6b** may be attributed to the higher electronegativity of nitrogen compared to that of arsenic. Compound **6b** was isolated in 38% yield after two weeks at room temperature. It was also obtained in ca. 40% yield from the reaction of $SeCl_4$ with 1-adamantylamine in a 1:6 molar ratio in diethyl ether. The crystal structure of **6b** is described below.

The resonance at 1213 ppm is assigned to OSe(μ-NAd)$_2$SeO (**2b**). The corresponding *tert*-butyl derivative OSe(μ-N^{t}Bu)$_2$SeO (**2a**) shows a resonance at 1242 ppm. The two signals of equal intensity at 1146 and 900 ppm are similarly assigned to the inequivalent selenium environments in OSe(μ-NAd)$_2$SeNAd (**4b**) [cf. $\delta(^{77}Se) = 1157$ and 882 for **4a** in hexane].

The hybrid imido−oxo selenium(IV) ring systems **2b** and **4b** are presumably formed by partial hydrolysis of the extremely moisture-sensitive selenium diimide **1b**. We have not been able to identify the compound(s) responsible for the resonances at 1102 and 811 ppm. We note, however, that the former falls in the range for an N**Se**Se selenium environment.[14]

X-ray Structure of $Se_3(NAd)_2$ (6b). An X-ray structural determination of **6b** revealed a five-membered $\overline{\mathrm{SeSeNSeN}}$ ring (Figure 2). Although five-membered rings are known for selenium−nitride systems, e.g., $Se_3N_2Cl^+$,[30−33] the heterocycle **6b** represents a previously unknown ring size for chalcogen imides. It is the first member of the homologous series $[Se_3(NR)_2]_n$ ($n = 1, 2, 3$) for which only the 15-membered ring Se$_9$(N^{t}Bu)$_6$ has been structurally characterized.[15] Herberhold and Jellen claimed the formation of "Se$_3$(N^{t}Bu)$_2$" from the decomposition of **1a**,[12] but subsequent studies showed that this product is Se$_9$(N^{t}Bu)$_6$.[14] This new finding suggests that the smaller oligomer [Se$_3$(N^{t}Bu)$_2$]$_n$ ($n = 1$ or 2), which was isolated from the reaction of $SeCl_2$ with *tert*-butylamine in THF,[14] is also a five-membered ring ($n = 1$). The structure of a related five-membered ring $Se_3(AsPh)_2$ has been reported.[29]

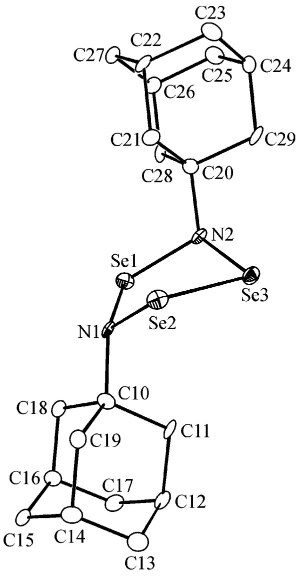

Figure 2. Molecular structure of $Se_3(NAd)_2$ (**6b**) showing the atomic numbering scheme.

The metrical parameters for **6b** are summarized in Table 2 and compared with those for other cyclic selenium imides in Table 3. The two Se−N bonds in the N(1)−Se(1)−N(2) fragment [1.892(4) and 1.881(4) Å] are significantly longer than those in the N(1)−Se(2)−Se(3)−N(2) fragment [1.846(4) and 1.860(5) Å]. The latter pair may be compared to the value of 1.834 Å for the Se−N−Se units in **5a**.[14] The Se−Se bond distance of 2.404(1) Å in **6b** is also markedly longer than the mean Se−Se bond lengths in Se$_9$(N^{t}Bu)$_6$ (2.336 Å)[15] and $Se_3(AsPh)_2$ (2.334 Å).[29] The elongated bonds are likely the result of ring strain in the five-membered ring, which is highly puckered with torsion angles ranging from 16.1(3)° to 46.7(2)° (see Table 2). The high value about the Se(2)−Se(3) bond presumably reflects the avoidance of lone pair−lone pair interactions on adjacent selenium atoms. The endocyclic bond angles at Se(2) and Se(3) are ca. 12° smaller than that at Se(1). The geometry at the nitrogen atoms is distinctly pyramidal ($\sum\angle N(1) = 343.0°$, $\sum\angle N(2) = 344.2°$) in marked contrast to the almost planar configuration at the nitrogen atoms in the chair-shaped six-membered ring **5a**.[14]

Structural Comparison of the Isoelectronic Series $(SeO_2)_\infty$, $(RNSeO)_2$, and $Se(NR)_2$. The structures of Se(NAd)$_2$ (**1b**) and *cis*-OSe(μ-N^{t}Bu)$_2$SeO (**2a**) were reported in a preliminary communication.[11] It is informative to consider the structural trends within the isoelectronic series, **1b**, **2a**, and **3**, in the context of the isovalent analogues formed by the other chalcogens (see Chart 2). The sulfur(IV) analogues of **1**, **2**, and **3** are, without exception, monomers.[1] By contrast, a trend from monomers through dimers to polymer is observed for the series of selenium(IV) imides and oxides.[34] The tendency to form singly

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[30] Siivari, J.; Chivers, T.; Laitinen, R. S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1518.

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[34] In the vapor phase selenium dioxide forms a dimeric species identified as *trans*-OSe(μ-O)$_2$SeO by a matrix IR study: Ozin, G. A.; Vander Voet, A. *J. Mol. Struct.* **1971**, *10*, 173.

Table 2. Selected Bond Lengths (Å), Bond Angles (deg) and Torsion Angles (deg) for $Se_3(NAd)_2$ (**6b**)

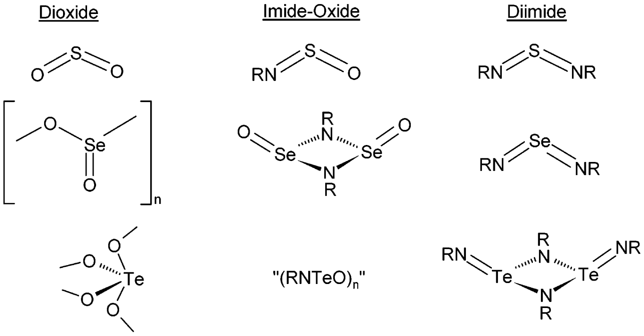
bond length		bond angle		torsion angle	
Se(1)−N(2)	1.881(4)	N(2)−Se(1)−N(1)	105.76(17)	N(1)−Se(2)−Se(3)−N(2)	46.7(2)
Se(1)−N(1)	1.892(4)	N(1)−Se(2)−Se(3)	93.95(14)	Se(3)−Se(2)−N(1)−Se(1)	−37.6(3)
Se(2)−N(1)	1.846(4)	N(2)−Se(3)−Se(2)	92.92(14)	N(2)−Se(1)−N(1)−Se(2)	16.1(3)
Se(2)−Se(3)	2.4044(8)	C(10)−N(1)−Se(2)	118.9(3)	Se(2)−Se(3)−N(2)−Se(1)	−41.7(2)
Se(3)−N(2)	1.860(5)	C(10)−N(1)−Se(1)	112.8(3)	N(1)−Se(1)−N(2)−Se(3)	23.4(3)
N(1)−C(10)	1.516(7)	Se(2)−N(1)−Se(1)	111.30(19)		
N(2)−C(20)	1.508(7)	C(20)−N(2)−Se(3)	120.0(3)		
		C(20)−N(2)−Se(1)	113.7(4)		
		Se(3)−N(2)−Se(1)	110.46(19)		

Table 3. Bond Lengths (Å) and Bond Angles (deg) for Cyclic Selenium Imides

ring system	*r*(Se−N)	*r*(Se−Se)	∠NSeN	∠NSeSe	∠SeNSe	∑∠N[a]
$Se_3(NAd)_2$	1.853(4)[b] 1.886(4)[b]	2.4044(8)	105.8(2)	93.5(1)	110.9(2)	343.6
$Se_9(N^tBu)_6$[c]		2.336(3)	101.0(7)	111.5(4)	114(1)	351
$Se_3(N^tBu)_3$[d]	1.831(8)[b]		106.6(2)		113.3(2)	358.9
$Se_6(N^tBu)_2$[c]	1.830(4)	2.333(1)		110.0(1)	114.8(2)	358.6

[a] Sum of angles at nitrogen atoms. [b] Mean value. [c] Reference 15. [d] Reference 14.

Chart 2. Multiple Bonding in Chalcogen(IV) Imides and Oxides



bonded molecules in preference to doubly bonded molecules is even more pronounced for tellurium. Tellurium(IV) diimides are dimeric[9,35] whereas tellurium dioxide is a three-dimensional polymer consisting of only Te−O single bonds.[36] Hybrid imido−oxo tellurium(IV) species (RNTeO)$_n$ are unknown, but a polymeric structure seems likely in view of the above trends and the propensity of telluroxides to dimerize, e.g., [^{t}BuNTe(μ-N^{t}Bu)$_2$(μ-O)]$_2$[37] and [OC(μ-N^{t}Bu)$_2$Te(μ-O)]$_2$.[38] We have recently isolated the tetramer OTe(μ-N^{t}Bu)$_2$Te(μ-O)$_2$Te(μ-N^{t}Bu)$_2$TeO by complexation of the terminal Te═O groups with $B(C_6F_5)_3$.[39]

A comparison of the structural parameters for selenium(IV) imides and oxides is given in Table 4.[40] For this series of compounds terminal Se═O bond lengths fall within the narrow range 1.62−1.63 Å (cf. 1.617(4) Å in OSe(NPPh$_3$)$_2$[43] and 1.612(5) Å in $OSeCl_2$).[44] The terminal Se═N(R) bond lengths are somewhat longer with a range 1.68−1.73 Å. For both SeO and SeN bonds, the difference between single and double bonds is ca. 0.19 Å.

Table 4. Bond Lengths (Å) for Selenium(IV) Imides and Oxides

compd	*r*(Se−O)	*r*(Se═O)	*r*(Se−N)	*r*(Se═N)	ref
$(SeO_2)_\infty$	1.8171(3)	1.631(3)			this work[b]
$(SeO_2)_\infty$	1.7951(1)	1.624(2)			13b[c]
OSe(*m*-N^{t}Bu)$_2$-SeO		1.621(2)	1.885(3)[a]		14
OSe(*m*-N^{t}Bu)$_2$-SeN^{t}Bu		1.628(4)	1.864(2)[a]	1.687(4)	14
			1.937(6)[a]		
$Se(NAd)_2$				1.679(8) 1.732(7)	11

[a] Mean value. [b] 173 K. [c] 139 K.

Cyclodimerization of Chalcogen Diimides and Related Cycloaddition Reactions. In order to provide further insights into the structural trends observed for multiply bonded chalcogen(IV) systems, we have calculated the gas-phase cyclodimerization energies for E(NR)$_2$ and RNEO (E = S, Se; R = H, Me, ^{t}Bu, SiMe$_3$) and cycloaddition energies for reactions in eqs 1−3 at different levels of theory.

$$\mathrm{RNSeO} + \mathrm{E(NR)_2} \rightarrow \mathrm{RNE}(\mu\text{-}\mathrm{NR})_2\mathrm{SeO} \tag{1}$$

$$\mathrm{RNSO_2} + \mathrm{Se(NR)_2} \rightarrow \mathrm{O_2S}(\mu\text{-}\mathrm{NR})_2\mathrm{SeNR} \tag{2}$$

$$\mathrm{S(NR)_2} + \mathrm{Se(NR)_2} \rightarrow \mathrm{RNS}(\mu\text{-}\mathrm{NR})_2\mathrm{SeNR} \tag{3}$$

The optimized structures of all molecules are given in Supporting Information. For all reaction products, the structural parameters are very similar in different conformations and are therefore reported only for the all-*cis*-conformation (conformation a in Chart 1) since it was found to be generally the most favorable in energy (see below).

In the case of sulfinyl and seleninylamines, the optimized geometries can be compared with experimental values determined for various RNSO structures. The optimized parameters agree reasonably well with the experimental values determined by electron diffraction[45] or microwave

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(35) Chivers, T.; Gao, X.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1994**, 2149.

(36) Beyer, H. *Z. Kristallogr.* **1967**, *124*, 228.

(37) Chivers, T.; Parvez, M.; Schatte, G. *Inorg. Chem.* **1999**, *38*, 5171.

(38) Schatte, G.; Chivers, T.; Jaska, C.; Sandblom, N. *Chem. Commun.* **2000**, 1657.

(39) Chivers, T.; Schatte, G. *Abstract*, *Tenth International Symposium on Inorganic Ring Systems*, Burlington, VT, August, 2003.

(40) During the course of this work, the structure of $(SeO_2)_\infty$ was redetermined. The structural parameters were similar to those reported in the 1992 paper[13b] (see Table 4). We note, however, that recent inorganic chemistry textbooks[41,42] quote Se−O and Se═O bond lengths of 1.78(3) and 1.73(8) Å, respectively, which are taken from the 1937 structural determination.[13a]

(41) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; Butterworth Heinemann: Oxford, U.K., 1997; p 779.

(42) Holleman, A. F.; Wiberg, E. *Inorganic Chemistry*, 34th ed.; Wiberg, N., Ed.; Academic Press: Berlin, 2001; p 583.

(43) Folkerts, H.; Dehnicke, K.; Maichle-Mössmer, C.; Strähle, J. Z. *Anorg. Allg. Chem.* **1995**, *621*, 1171.

(44) Gregory, D.; Hargittai, I.; Kolonits, M. *J. Mol. Struct.* **1976**, *31*, 261.

(45) Gobbato, K. I.; Della, V.; Carlos, O.; Oberhammer, H. *J. Mol. Struct.* **1995**, *350*, 227.

spectroscopy.[46−48] As found for sulfur and selenium diimides,[25] *syn*-E═N bonds are shorter than *anti*-E═N bonds, *syn*-ENA (A = H, C, or Si) bond angles are wider than *anti*-ENA bond angles, and ENA bond angles in selenium compounds are narrower than those in the corresponding sulfur compounds. The structural trends in sulfinyl and seleninylamines seem to depend mainly on steric factors with electronic factors playing only a minor role.

The optimized bond parameters of the dimerization and cycloaddition products (eqs 1−3) can be compared with the experimental values[11,14] and with the molecular parameters that have been observed for monomeric sulfur[49] and selenium diimides.[11] The calculated parameters are found to be close to the experimental values, where available: the RMS deviation between the calculated and observed bond lengths is only 0.023 Å and that of the bond angles is 3°.

In sulfur and selenium dimers, the exocyclic chalcogen−nitrogen bond lengths (EN) are in a good agreement with experimental values for the EN double bonds in monomeric chalcogen(IV) diimides. The endocyclic chalcogen−nitrogen bonds are predicted to be ca. 0.2 Å longer than the exocyclic chalcogen−nitrogen bonds for both sulfur and selenium diimide dimers, indicating that the bonds in the ENEN ring are single bonds. This is consistent with the experimental observations. The endocyclic EN bonds are systematically shorter in $O_xE(\mu\text{-}NR)_2SeNR$ (E = S, Se; $x = 1, 2$) than in the corresponding diimide dimers. The bond parameters in the ENEN rings in different dimerization products are rather similar, as exemplified by the endocyclic bond angles ∠SNS = 98.6−102.0° and ∠SeNSe = 96.8−102.1°. The endocyclic bond angles ∠NEN span a range of 77.2−80.7° and 76.8−82.6° in sulfur and selenium compounds, respectively. By contrast, the torsion angle τ_{ENEN} expectedly depends on the size of the exocyclic substituent. Similar trends in structural parameters are also observed for all calculated cycloaddition structures.

Total energies for all molecules calculated at MP2/cc-pVDZ//B3PW91/6-31G*, CCSD/cc-pVDZ//B3PW91/6-31G*, and CCSD(T)/cc-pVDZ//B3PW91/6-31G* levels of theory are presented in Supporting Information. The *syn*-conformation for the monomeric sulfinyl and seleninylamines appears to be more stable than the *anti*-conformation. This is in agreement both with the experimental observations[45−48] and previous theoretical calculations.[50] At the CCSD(T)/cc-pVDZ//B3PW91/6-31G* level of theory, the *syn*-conformation is 25 and 30 kJ mol^{-1} more stable for sulfur and selenium compounds, respectively. This conformational preference has been rationalized in terms of the interactions between the nitrogen lone pair and chalcogen p and d orbitals.[10,50]

Table 5. Cylcodimerization Energies of $E(NR)_2$ and RNEO (E = S, Se; R = H, Me, ^{t}Bu, $SiMe_3$) (kJ mol^{-1})[a]

	H	Me	^{t}Bu	$SiMe_3$
$2RNSNR \rightarrow RNS(\mu\text{-}NR)_2SNR$[b]				
MP2/cc-pVDZ	120	98	105	67
CCSD/cc-pVDZ	102	83		
CCSD(T) /cc-pVDZ	114	91		
$2RNSeNR \rightarrow RNSe(\mu\text{-}NR)_2SeNR$[b]				
MP2/cc-pVDZ	40	24	25	−28
CCSD/cc-pVDZ	4	−8		
CCSD(T) /cc-pVDZ	23	7		
$2RNSO \rightarrow OS(\mu\text{-}NR)_2SO$				
MP2/cc-pVDZ	83	66	60	46
CCSD/cc-pVDZ	65	50	42	26
CCSD(T) /cc-pVDZ	77	60	52	34
$2RNSeO \rightarrow OSe(\mu\text{-}NR)_2SeO$				
MP2/cc-pVDZ	−6	−19	−26	−48
CCSD/cc-pVDZ	−38	−42	−56	−83
CCSD(T) /cc-pVDZ	−18	−25	−38	−66

[a] Values include unscaled zero point energy corrections. [b] Density functional calculations gave values of 34.9 and −2.8 kJ mol^{-1} for E = S and E = Se, respectively.[10]

For most cyclodimerization and cycloaddition products, the conformation with the lowest energy was found to be all-*cis*-conformation (a in Chart 1). The experimental information is restricted to ^{t}Bu derivatives which all adopt the conformation in which the exocyclic and endocyclic R groups are mutually *cis*, but on opposite sides of the ENEN ring (conformation b in Chart 1). The difference in the experimental and calculated conformational preference can, however, be explained by noting that the theoretical calculations do not take packing effects into account and that the energies of different conformations are in general very close to each other.[51] In the case of tellurium diimide dimers, both *cis* and *trans* conformers have been observed and structurally characterized,[9,35] but the *trans* conformer is known to convert into the *cis* conformer in solution at room temperature.[52]

The [2 + 2] cyclodimerization energies of sulfur and selenium diimides and sulfinyl- and seleninylamines are presented in Table 5, and the corresponding energies of various cycloaddition reactions (eqs 1−3) are in Table 6.[53] It can be seen from Tables 5 and 6 that the theoretically most reliable CCSD(T) reaction energies fall between the MP2 and CCSD values and are 10−20 kJ mol^{-1} smaller than

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(46) Kirchhoff, W. H. *J. Am. Chem. Soc.* **1969**, *91*, 2437.

(47) Rao, V. M.; Yardley, J. T.; Curl, R. F. *J. Chem. Phys.* **1965**, 42, 284.

(48) The different structure determinations of MeNSO have produced slightly different molecular parameters: Beagley, B.; Chantrell, S. J.; Kirby, R. G.; Schmidling, D. G. *J. Mol. Struct.* **1977**, *36*, 55.

(49) See ref 25 and references therein.

(50) See for example: Ehrhardt, C.; Ahlrichs, R. *Chem. Phys.* **1986**, *108*, 417.

(51) For example, the relative energies of all conformations of the same molecule of various ^{t}Bu derivatives span only a small energy range of 15 kJ mol^{-1}.

(52) Chivers, T.; Gao, X.; Parvez, M. *Inorg. Chem.* **1996**, *35*, 9.

(53) The reaction energies were not corrected for the basis set superposition errors (BSSE). This is mainly due to the fact that the generally used counterpoise correction (CP) procedure[54a] is rigorously defined only in the case of weakly bound complexes. In addition, the truncated basis set calculations also include an error arising from the general incompleteness of the basis set (BSIE). These two errors have opposite signs and tend to cancel each other partially in the case of smaller basis sets. To gain insight in the reliability of the calculated values, we carried out model calculations on the cyclodimerization and cycloaddition energetics of $E(NH)_2$ and HNEO (E = S, Se) by using a more flexible cc-pVTZ basis set (see Supporting Information). In general, the cc-pVTZ reaction energies were found to be ca. 30 kJ mol^{-1} lower than the corresponding cc-pVDZ values. However, the correction for BSSE was estimated to increase the cc-pVTZ energies by ca. 25 kJ mol^{-1}. Therefore, the non-BSSE corrected cc-pVDZ energies perform adequately in the semiquantitative consideration of trends in reaction energies. For discussion of BSSE in tightly bound systems, see for example refs 54b−d.

Table 6. Energies of Various Asymmetric [2 + 2] Cycloaddition Reactions (kJ mol^{-1})[a]

	H	Me[b]	^{t}Bu	SiMe$_3$
RNSeO + RNSNR → OSe(μ-NR)$_2$SNR				
MP2/cc-pVDZ	56	39	40	8
CCSD/cc-pVDZ	31	20		
CCSD(T) /cc-pVDZ	46	32		
RNSeO + RNSeNR → OSe(μ-NR)$_2$SeNR				
MP2/cc-pVDZ	18	1	−1	−40
CCSD/cc-pVDZ	−16	−26		
CCSD(T) /cc-pVDZ	3	−10		
RNSO$_2$ + RNSeNR → O$_2$S(μ-NR)$_2$SeNR				
MP2/cc-pVDZ	−20	−53	−53	−73
CCSD/cc-pVDZ	−46	−76		
CCSD(T) /cc-pVDZ	−30	−64		
RNSNR + RNSeNR → RNS(μ-NR)$_2$SeNR				
MP2/cc-pVDZ	80	62	67	19
CCSD/cc-pVDZ	53	38		
CCSD(T) /cc-pVDZ	69	50		

[a] Values include unscaled zero point energy corrections.

the MP2 values. While it was not possible to carry out CCSD and CCSD(T) calculations for all molecular systems, the trends can been utilized to produce energy estimates for these levels of theory, as shown in Figure 3.[55]

For sulfur diimides, the reaction energies are found to be positive at all levels of theory, thereby indicating an endothermic process. For selenium diimides, the process is predicted to be energetically neutral, the signs of the energy values being somewhat dependent on the level of theory.[56] This is consistent with the experimental observations that **1a** and **1b** are monomeric species.[8,11] The difference in reaction energies for sulfur and selenium diimides can be ascribed to the lower π-bond energies of Se═N bonds, which make the coupling of the two fragments energetically more preferable.[10]

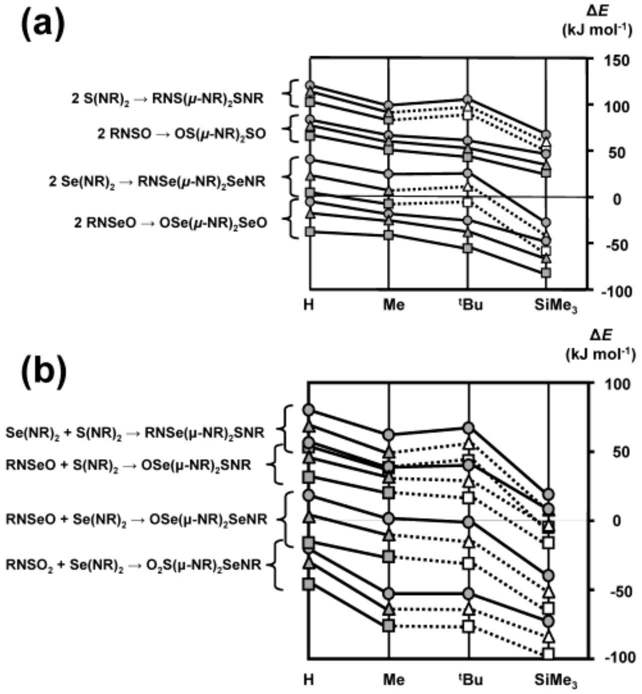

Figure 3. The trends in the energies of (a) cyclodimerization reactions and (b) cycloaddition reactions at different correlated levels of theory: reaction energies calculated at MP2/cc-pVDZ//B3PW91/6-31G* level of theory (●), reaction energies calculated at CCSD/cc-pVDZ//B3PW91/6-31G* level of theory (■), reaction energies calculated at CCSD(T)/cc-pVDZ//B3PW91/6-31G* level of theory (▲), estimates based on the trends calculated by the above-mentioned MP2, CCSD, and CCSD(T) calculations (□, △).[56]

Figure 3 shows that the cyclodimerization and cycloaddition energies are rather independent of the identity of the R group (H, Me, and ^{t}Bu derivatives). However, according to the present calculations the reaction energies of SiMe$_3$ derivatives behave anomalously. For example, the cyclodimerization energy of Se(NSiMe)$_3$ is negative at all levels of theory. This derivative has been reported as a dark red oil,[57] but the solid-state structure is unknown. It is a useful synthon for different Se−N heterocycles.[58] The origin of the anomalous behavior of trimethylsilylamines has been discussed on several occasions.[59] It has been attributed to bonding interactions, and consequent charge delocalization, involving N 2p lone pair orbitals and either empty Si 3d orbitals or Si−C σ* orbitals (negative hyperconjugation).

As indicated in Table 5 and Figure 3a, the cyclodimerization energies for RNSeO are negative at all levels of theory, in agreement with the observed stability of **2a**.[11] By contrast, the cyclodimerization energies for RNSO are clearly positive, which is consistent with the observed monomeric structures of sulfinylamines. It can also be seen from Table 5 that the reaction energies are lower for the chalcogen imido−oxo systems than for the corresponding diimides. The observed trend most likely originates from the high electronegativity of oxygen which results in further destabiliza-

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(55) The trends in the reaction energetics at different correlated levels of theory seem to depend mainly on the identity of the chalcogen atoms in the molecule. By considering energy values of the molecules that could be calculated at all three correlated levels, the semiquantitative contributions of one sulfur and selenium atom (C_E, E = S, or Se) to the correction of the reaction energies could be established, as follows, for MP2 → CCSD: $C_S = -9(1)$ kJ mol^{-1}, $C_{Se} = -15(2)$ kJ mol^{-1}. For MP2 → CCSD(T), $C_S = -4(1)$ kJ mol^{-1}, $C_{Se} = -7(2)$ kJ mol^{-1}. It can be seen from Figure 3 that these contributions establish reasonable estimates for the CCSD/cc-pVDZ//B3PW91/6-31G* and CCSD(T)/cc-pVDZ//B3PW91/6-31G* reaction energies, when the corresponding MP2/cc-pVDZ//B3PW91/6-31G* energy values are known.

(56) Reaction energies have only been calculated at highly correlated levels of theory, since the inclusion of electron correlation was found to be critical in order to obtain a proper description of the energetics of the studied systems. The lower level methods HF/6-31G*, MP2/6-31G*, and B3PW91/6-31G* predict significantly less positive energies for the cyclodimerization. Whereas in the case of sulfur diimides both correlated and uncorrelated calculations imply strongly endothermic processes, the inclusion of electron correlation is rather critical in the case of selenium diimides. The uncorrelated methods of theory indicate that the cyclodimerization of selenium diimides is exothermic. When electron correlation is taken into account, the reaction energies of selenium diimides become approximately zero or slightly negative, indicating an energetically neutral process.

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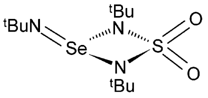
(58) Bestari, S. K.; Cordes, A. W.; Oakley, R. T.; Young, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 2249.

(59) (a) Beach, D. B.; Jolly, W. L. *Inorg. Chem.* **1984**, *23*, 4774. (b) Reed, A. E.; Schade, C.; Schleyer, P. V.; Kamath, P. V.; Chandrasekhar, J. *Chem. Commun.* **1988**, 67. (c) Mo, Y.; Zhang, Y.; Gao, J. *J. Am. Chem. Soc.* **1999**, *121*, 5737.

tion of the chalcogen nitrogen double bond. This conclusion is supported by the energy decomposition analysis which reveals preparation energies that are ca. 40 kJ mol^{-1} smaller for imido−oxo systems than for the corresponding diimides.

The cycloaddition energies for reaction 1 (E = Se) are also slightly negative [see Table 6 and Figure 3b], consistent with the observed structure of **4a**.[14] Negative reaction energies are also predicted for the cycloaddition reactions (2), consistent with the formation of the selenium(IV)−sulfur(VI) species **7**.[14] Finally, we note that the cycloaddition energies are found to be positive for all reactions where one of the reagents is a sulfur(IV) diimide, e.g., eq 3.



7

Conclusions

The thermal decomposition of $Se(NAd)_2$ (Ad = 1-adamantyl) in THF leads to the formation of the novel cyclic selenium imide $Se_3(NAd)_2$ together with the six-membered $Se_3(NAd)_3$, and the partial hydrolysis products $AdNSe(\mu\text{-}NAd)_2SeO$ and $OSe(\mu\text{-}NAd)_2SeO$. The recently reported X-ray structures of $(AdN)_2Se$, $^tBuNSe(\mu\text{-}N^tBu)_2SeO$, $OSe(\mu\text{-}N^tBu)_2SeO$, and $(SeO_2)_\infty$ allow a comparison of structural trends within the isoelectronic series spanning from selenium(IV) diimides to selenium(IV) dioxide. Selenium diimides are monomeric, while the hybrid imido−oxo species are dimeric and selenium dioxide is a two-dimensional polymer with SeO single and double bonds. The sulfur(IV) analogues of **1**, **2**, and **3** are, without exception, monomers. However, the tendency to form singly bonded molecules in preference to doubly bonded molecules is even more pronounced for tellurium than for selenium. Tellurium(IV) diimides are dimeric, and tellurium dioxide is a three-dimensional polymer consisting of only Te−O single bonds.

Theoretical calculations for the energetics of the [2 + 2] cyclodimerization and cycloaddition reactions predict both sulfur(IV) and selenium(IV) diimides to be monomeric with the sole exception of $Se(NSiMe_3)_2$ that may show a tendency to dimerize. The cyclodimerization of RNSeO and the cycloaddition of RNSeO with $Se(NR)_2$ as well as that of $RNSO_2$ with $Se(NR)_2$ are energetically favored processes consistent with the observed structures of $OSe(\mu\text{-}N^tBu)_2SeO$, $OSe(\mu\text{-}N^tBu)_2SeN^tBu$, and $O_2S(\mu\text{-}N^tBu)_2SeN^tBu$, respectively. However, the calculations indicate that cycloaddition is unlikely when one of the reactants is sulfur(IV) diimide.

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Supporting Information Available: Two X-ray crystallographic files in CIF format and 12 tables of optimized geometries and energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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