Mo (dz², dxz) S(px)   Mo (dxz,dz²) S (pz,s)   Mo (dyz) S (py)

Co (dyz,dx²-y²) S (py)   Co (dyz,dx²-y²) S (pz, s)   Co (dxz) S (px)

Figure 4. Principal orbital interactions of the μ_4-S atom in $Cp_2Mo_2Co_2S_3(CO)_4$. Diagrams are arranged in the order of descending overlap populations for each M/S interaction.

over the Mo2-Co1-Co2 face.[36]

Teo's equation can be modified for inclusion of main-group elements in the cluster framework as VSE = 2[8(TM) + 2(MG) − F + 2 + X], where TM = number of transition-metal vertices and MG = number of main-group vertices. The factor "2" is derived by ignoring exopolyhedral bonds to or lone pairs on the main-group vertex atoms.[37] Thus, the Mo_2Co_2S core in **4** requires 2[8(4) + 2(1) − 6 + 2 + X] = 60 + 2X VSE (X = 0 or 2). The observed 60-VSE count in **4** is consistent with a value of X = 0, and clusters **3** and **4** have comparable electronic structures. This might be anticipated by noting that the $Co(CO)_3$ fragment is isolobal with S (three orbitals used for constructing the cluster framework in each case), but the former fragment contributes 1 less electron (3) than the sulfur atom (4).

It is interesting to note that the $Mo_2Co_3S_2$ and $Mo_2Co_2S_3$ cores can be treated as bicapped trigonal bipyramids (i.e., counting the μ_3-sulfur atoms as part of the cluster framework), using Teo's equation as modified above. For the M_5S_2 core, VSE = 2[8(5) + 2(2) − 10 + 2 + X] = 72 + 2X, and for M_4S_3 core, VSE = 2[8(4) + 2(3) − 10 + 2 + X] = 60 + 2X. That the VSE re-

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quirements are identical with those based on a trigonal bipyramid with the μ_3-S ligands merely donating 4 electrons to the total electron count reflects the well-known fact that capping a triangular face of a cluster does not change the electron count.

The core of cluster **6**, $Mo_2Fe_3S_4$, is formed from two edge-shared square pyramids. Apparently, this structural feature has not been observed in all-metal, M_8 clusters and is extremely rare even for metal-heteroatom clusters. Teo's rule 6 states that X = number of shared edges; in this case X = 1, and VSE = 2[8(8) − 10 + 2 + X] = 112 + 2X = 114 for an all-metal cluster. For the M_4S_4 core, we have VSE = 2[8(4) + 2(4) − 10 + 2 + X] = 64 + 2X = 66 for X = 1. The observed electron count for **6** is 66.

These results suggest that μ_3- and μ_4-sulfido ligands can be considered to be an integral part of the cluster polyhedron and that there exists a very close relationship between the geometries and electronic structures of M_nS_x clusters and the corresponding M_{n+x} all-metal clusters.

In the treatment, both μ_3- and μ_4-sulfido ligands were considered to donate 4 electrons to the cluster VSE count. As part of our ongoing studies on the electronic structures of metal sulfido clusters, we had occasion to perform EHMO studies of cluster **4**.

Here, we briefly mention the main features of the bonding of μ_3- and μ_4-sulfido ligands: (1) mostly S atomic p orbitals are used, although a significant fraction of the overlap populations involve sulfur 3s orbitals; (2) in **4**, the overlap populations are fairly evenly divided between Co–S (40%) and Mo–S (60%) bonds; (3) the total M–S overlap population to the μ_4-S atom is 1.55 compared to 1.57 for the metal–μ_3-S bonds (this suggests both μ_3- and μ_4-S donate the same number of electrons). The fact that the same overlap population is spread over four M–S bonds in the μ_4 ligand rather than concentrated in three bonds in the μ_3 ligand provides the rationale for the longer μ_4-S to metal bonds. The principal orbital interactions are illustrated in Figure 4.

Conclusions. $Cp_2Mo_2(SR)_2(CO)_2$ derivatives have been shown to be useful precursors to new bimetallic sulfido clusters. A modification of Teo's topological equation to include main-group vertices shows the close similarity of geometries of sulfido clusters and all-metal cluster cores.

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Redox Chemistry of Diphenyl Diselenide and Its Chemistry in the Presence of Protons, Hydroxide, Water, and Hydrogen Peroxide

Andrzej Sobkowiak and Donald T. Sawyer*

In acetonitrile, diphenyl diselenide (PhSeSePh) undergoes a reversible one-electron reduction (−0.85 V vs SCE), which is similar to the electrochemical behavior of dioxygen. PhSeSePh facilitates the oxidation of water and hydroxide ion and the reduction of protons. In combination with HOOH, PhSeSePh is photocatalyzed and proton-catalyzed to form a 1:1 adduct, which reacts with two more HOOH molecules to form two PhSe(O)OH molecules. This adduct adds to olefins (RCH=CHR') to form RCH(OH)CH(SePh)R'.

The chemistry of organoselenium compounds has been extensively investigated because of their utility in organic synthesis.[1-3]

Barton and co-workers[4] have demonstrated that the Gif system (iron catalyst, O_2, zinc dust, acetic acid, and pyridine) for the

selective transformation of methylenic carbons to ketones,[5,6] when done in the presence of diphenyl diselenide (PhSeSePh), yields phenylselenyl derivatives of the hydrocarbon substrates at the expense of the ketonization process. A recent study[7] has shown that in a pyridine/acetic acid solvent the combination of iron(II) bis(picolinate) [Fe(PA)$_2$], hydrogen peroxide, PhSeSePh, and a hydrocarbon (RH; e.g., cyclohexane) (2:2:1:100 mole ratio) reacts stoichiometrically to give 2 equiv of the phenylselenyl derivatives of the substrate [e.g., 2 (c-C$_6$H$_{11}$)SePh].

Selenenic acids (RSeOH) add to olefins to give β-hydroxy selenides, which can be selectively transformed to epoxides, allyl alcohols, α,β-unsaturated carbonyl compounds, alcohols, olefins, and α-selenocarbonyl compounds.[8-10] This selenenylating reagent [normally produced by the reduction of the corresponding seleninic acid (RSe(O)OH)] also has been generated electrochemically via reduction of PhSeSePh in the presence of alcohols and water.[11] Electrochemical oxidation of PhSeSePh in the presence of an alkane in an acetonitrile solution yields acetamidoselenides,[12] with the electro-generated phenylselenium cation as the initiator (cyclohexane yields mainly 2-acetamido-1-(phenylsenenyl)cyclohexane). Early polarographic studies[13-15] of PhSeSePh indicate that it reacts with the mercury electrode prior to electron transfer.

Experimental Section

Equipment. Cyclic voltammetry was accomplished with a Bioanalytical Systems Model CV-27 voltammetric controller and a Houston Instruments Model 100 XY recorder. These measurements were made with a 10-mL microcell assembly that was adapted for the working electrode, a Bioanalytical Systems glassy-carbon electrode (area 0.09 cm^2), a platinum-wire auxiliary electrode (contained in a glass tube with a medium-porosity glass frit and filled with a solution of supporting electrolyte), and a Ag/AgCl reference electrode (filled with aqueous tetramethylammonium chloride solution and adjusted to 0.00 V vs SCE) with a solution junction via a Pyrex glass tube closed with a cracked soft-glass bead that was contained in a Luggin capillary. The cyclic voltammograms were initiated at the rest potential of the solution, and voltages are reported versus SCE. The solutions contained 0.1 M tetramethylammonium perchlorate [TEAP] as the supporting electrolyte. The kinetic measurements for the PhSeSePh reaction with HOOH made use of a Hewlett-Packard Model HP 8450A diode-array rapid-scan spectrophotometer. The reaction products were analyzed with a Hewlett-Packard Model HP 5890 capillary-column gas chromatograph and a mass-selective detector. All measurements were made at 24 ± 1 °C.

Chemicals and Reagents. The reagents for the investigations were the highest purity commercially available and were used without further purification. Tetraethylammonium perchlorate (TEAP, GFS Chemicals) was vacuum-dried for 24 h prior to use. Tetrabutylammonium hydroxide [(Bu$_4$N)OH] was obtained from Aldrich as a 1 M solution in methanol; its concentration was determined by acid–base titration. Acetonitrile (Burdick and Jackson Laboratories; UV grade, <0.003% H$_2$O) and water (resistivity, 18 MΩ) from a Barnstead water-purification system were used for all of the measurements; high-purity argon gas was used to deaerate the solutions.
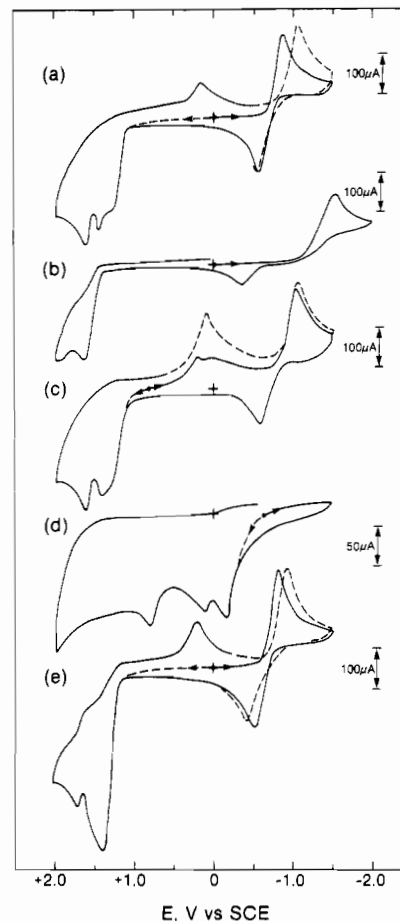
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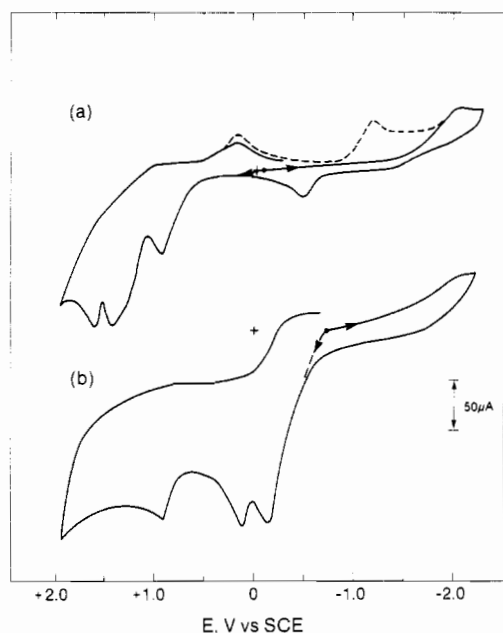(15) Paliani, G.; Cataliotti, M. L. *Z. Naturforsch.* **1974**, *29B*, 376.

Figure 1. Cyclic voltammograms of solutions in MeCN (0.1 M TEAP): (a) 5 mM PhSeSePh; (b) 5 mM PhSSPh; (c) 5 mM PhSeSePh plus 5 mM HClO$_4$; (d) 1 mM PhSeSePh plus 12 mM (Bu$_4$N)OH; (e) 5 mM PhSeSePh plus 60 mM H$_2$O. Conditions: scan rate 0.1 V s^{-1}; glassy-carbon working electrode (0.09 cm^2); SCE vs NHE, +0.242 V. Dashed line shows the initial anodic scan.

Results

Cyclic Voltammetry of PhSeSePh. Figure 1a (solid line) illustrates the cyclic voltammogram of PhSeSePh in acetonitrile, which exhibits a reversible reduction couple at −0.85 V and two irreversible oxidation peaks (+1.35 and +1.6 V). After an initial positive scan (Figure 1a, dashed line), scan reversal yields a new reduction peak at −1.1 V in place of the −0.85-V peak. For comparison, the cyclic voltammogram for diphenyl disulfide (PhSSPh) is included (Figure 1b). When an equimolar amount of hydrogen ions is present in the PhSeSePh solution, the rest potential is shifted from 0.0 to +0.85 V, and a one-electron-reduction peak at +0.1 V is observed with a second reduction at −1.1 V (there is no peak at −0.85 V). There are no changes in the potentials of the oxidation peaks, but the peak at +1.35 V becomes broader (Figure 1c). The presence of (Bu$_4$N)OH causes the reduction peak at −0.85 V to decrease in height and to disappear when the mole ratio (−OH:PhSeSePh) is 2:1 or greater. The presence of −OH results in an new oxidation peak at −0.2 V, which increases in height up to a mole ratio (−OH:PhSeSePh) of 12 (Figure 1d). For higher mole ratios, a peak due to free −OH appears (+0.55 V) and the oxidation peaks at +1.35 and +1.6 V are no longer present, but two new oxidation peaks at +0.15 and +0.9 V appear. Addition of water to PhSeSePh solutions does not affect the reversible reduction couple (−0.85 V), but causes the peak current for the oxidation at +1.35 V to increase (as well as the reduction current for the peak at +0.1 V upon scan reversal) and that for the peak at +1.6 V to decrease (Figure 1e). Controlled-potential electrolysis at +1.4 V of an acetonitrile solution that contains 5 mM PhSeSePh and 60 mM H$_2$O yields dioxygen (>60% efficient; O$_2$ assayed in product solution by cyclic voltammetry).

Figure 2. Cyclic voltammograms of solutions in MeCN (0.1 M TEAP): (a) 3 mM PhSeH; (b) 3 mM PhSeH plus 18 mM (Bu$_4$N)OH. Conditions: scan rate 0.1 V s^{-1}; glassy-carbon working electrode (0.09 cm^2); SCE vs NHE, +0.242 V. Dashed line shows the initial anodic scan.

Cyclic Voltammetry of PhSeH. An initial negative voltammetric scan for PhSeH yields a broad reduction peak at −2.0 V (Figure 2a), and an initial positive scan results in two oxidation peaks at −0.45 V (this peak does not appear when the negative scan is reversed before −2.0 V) and +0.95 V, as well as two oxidation peaks that are identical with those for the oxidation of PhSeSePh (+1.35 and +1.6 V). Scan reversal of an initial positive scan yields reduction peaks at +0.1 and −1.1 V.

Addition of 6 equiv of (Bu$_4$N)OH per PhSeH gives a solution with electrochemistry that is illustrated by the cyclic voltammogram of Figure 2b (three anodic peaks at −0.2, +0.15, and +0.9 V). With increased ratios of ⁻OH, a peak for its oxidation appears (+0.55 V).

Reaction of PhSeSePh with HOOH. Solutions of PhSeSePh in acetonitrile have an absorption band at 329 nm (Figure 3, inset), which can be used to monitor the reaction between PhSeSePh and HOOH. Figure 3 illustrates the reaction course for various HOOH: PhSeSePh mole ratios as well as the effect of photolytic and protic activation of PhSeSePH. Each of the curves is typical for an autocatalytic process. Stoichiometric studies establish that 3 mol of HOOH reacts with 1 mol of PhSeSePh.

Reaction of PhSeSePh with HOOH (1:1) in the Presence of Excess Cyclohexene. Combination of 0.1 M cyclohexene with 20 mM PhSeSePh and 20 mM HOOH results in the formation of 2-(phenylselenyl)cyclohexanol as the only product (however, even after 54 h, some PhSeSePh remains in the solution). With 0.2 mM HClO$_4$ present, the reaction rate is accelerated such that within 24 h all of the PhSeSePh is consumed to give a stoichiometric yield of product (40 mM).

Discussion and Conclusions

Table I summarizes the electron-transfer pathways and the redox potentials for PhSeSePh and PhSeH and for PhSeSePh and PhSeH in the presence of protons, ⁻OH, and water. The reversible electrochemical reduction of PhSeSePh clearly is different from the irreversible reduction of PhSSPh (Figure 1a, b) and appears to be similar to the reduction of dioxygen in aprotic media.[16] The latter similarity is consistent with a degree of π-bonding in PhSeSePh (as in the O$_2$ molecule)

$$[\text{Ph—}\overset{..}{\underset{..}{\text{Se}}}\text{—}\overset{..}{\underset{..}{\text{Se}}}\text{—Ph} \leftrightarrow \text{Ph—}\overset{..}{\underset{..}{\text{Se}}}\text{≡}\overset{..}{\underset{..}{\text{Se}}}\text{—Ph}] \quad (1)$$

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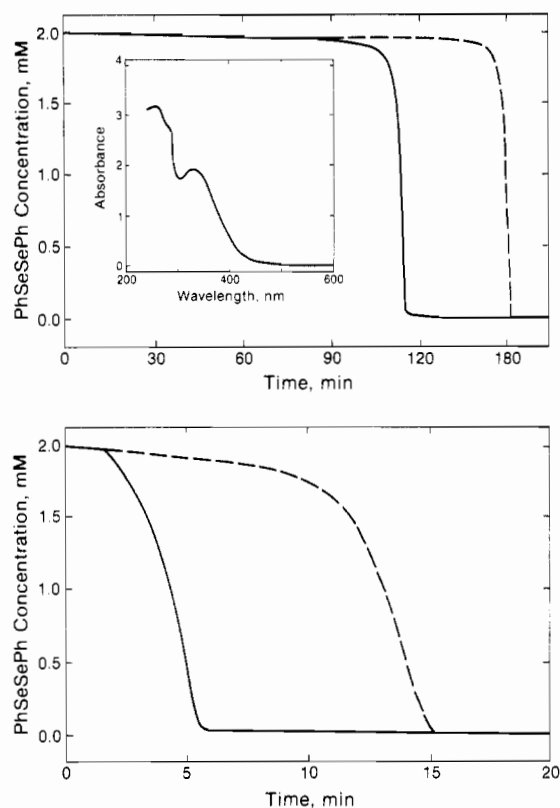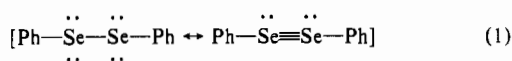

Figure 3. Concentration of PhSeSePh as a function of time of reaction for 2 mM PhSeSePh in MeCN solvent with (a) 6 mM HOOH, (b) 40 mM HOOH, (c) 40 mM HOOH (PhSeSePh solution photolyzed with 254-nm light for 30 min prior to the reaction), and (d) 40 mM HOOH plus 0.1 mM HClO$_4$. Inset: UV spectrum of 2 mM PhSeSePh in MeCN.

Table I. Redox Reactions in MeCN (0.1 M TEAP) of PhSeSePh and PhSeH and Reactions of PhSeSePh and PhSeH in Combination with HClO$_4$, (Bu$_4$N)OH, and H$_2$O

redox couple	$E_{1/2}$, V vs SCE
PhSeSePh + e$^-$ ⇌ PhSė–SePh	−0.85
PhSSPh + 2e$^-$ → 2PhS$^-$	−1.5
O$_2$ + e$^-$ ⇌ O$_2$·$^-$	−0.95
PhSeH + e$^-$ → PhSe$^-$ + H·	−2.0
PhSeH → PhSe· + H$^+$ + e$^-$	+0.9
$\quad \llcorner$⟶ $^1/_2$PhSeSePh	
PhSeSePh + H$^+$ + e$^-$ → [PhSeHSėPh] → $^1/_2$[PhSe(H)SePh]$_2$	+0.1
[PhSe(H)SePh]$_2$ + e$^-$ → PhSė–SePh + 2PhSeH	−1.1
PhSe$^-$ + 6⁻OH → PhSe(O)$_2$O$^-$ + 3H$_2$O + 6e$^-$	+0.2
4PhSeSePh + 2H$_2$O → 4PhSeSePh(H)$^+$ + O$_2$ + 4e$^-$	+1.35

The Se–Se bond length in the PhSeSePh molecule is 2.29 Å,[17] whereas the single-bond length between two divalent selenium atoms is 2.34 Å,[18] which infers that there is about 10% triple-bond character in PhSeSePh.

In the presence of PhSeSePh the reduction of protons is facilitated (+0.1 V rather than −1.9 V in the absence of PhSeSePh) via stabilization of the H· atom (PhSeHSėPh), which is analogous to the reduction of protons in the presence of O$_2$ to give HOO·.[19] However, (PhSeHSėPh) dimerizes; the dimer is reduced at −1.1
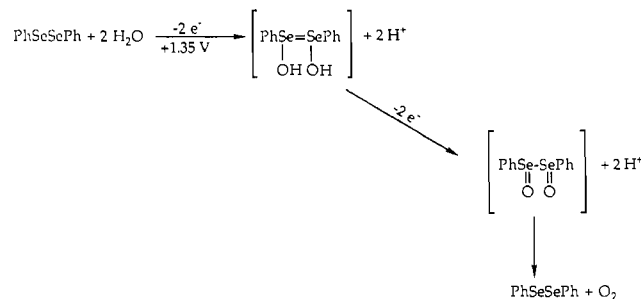
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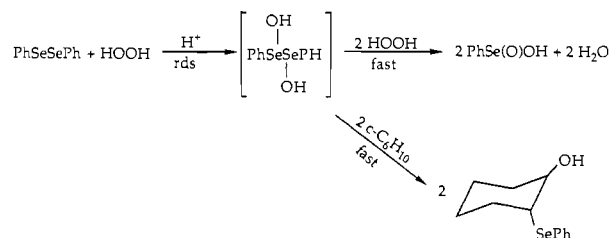(19) Cofré, P.; Sawyer, D. T. *Anal. Chem.* **1986**, *58*, 1057.

**Scheme I.** PhSeSePh-Catalyzed Electrooxidation of Water

**Scheme II.** 1-(PhSe)-2-OH Derivatization of Cyclohexene

V to give PhSeSePh and PhSeH (Table I).

The electrochemical behaviors of PhSeSePh and PhSeH in the presence of ⁻OH are similar (Figures 1d and 2b), and the elimination of the reduction peak for PhSeSePh after the addition of 2 equiv of ⁻OH indicates that reductive hydrolysis occurs.[20]

$$2PhSeSePh + 4^-OH \rightarrow 3PhSe^- + PhSe(O)O^- + 2H_2O \quad (2)$$

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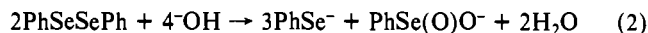
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Such formation of PhSe⁻ accounts for the analogous electrochemistry of PhSeSePh and PhSeH in the presence of excess ⁻OH. Oxidation of PhSe⁻ in the presence of excess ⁻OH occurs at +0.2 V, and the peak current increases with ⁻OH concentration up to a mole ratio of 6:1 (Table I) to give PhSe(O)₂O⁻ as the sole product. Thus, the combination of 12 ⁻OH per PhSeSePh is electrooxidized at +0.2 V via a 10-electron process.

$$PhSeSePh + 12^-OH \rightarrow 2PhSe(O)_2O^- + 6H_2O + 10e^- \quad (3)$$
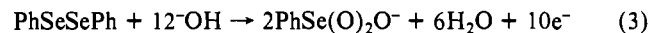
Oxidation of PhSeH at +0.9 V yields PhSeSePh and protons, which in combination are reduced at +0.05 V (Table I). In contrast, oxidation of PhSeSePh in the presence of excess water at +1.35 V yields dioxygen. A reasonable mechanistic pathway is outlined in Scheme I.

Scheme II presents plausible reaction pathways for the photolytic- and proton-induced oxygenation of PhSeSePh by HOOH, with formation of the 1:1 adduct being the rate-determining step. This adduct reacts with two more HOOH molecules to form PhSe(O)OH. When excess olefin is present, it reacts with the [PhSe(OH)Se(OH)Ph] adduct to give the 1-(PhSe)-2-OH derivatives of the olefin.

In summary, PhSeSePh is a versatile redox catalyst for the reduction of protons, the oxidation of water, and, in combination with HOOH, the derivatization of olefins. A previous report[7] discusses its utility as a trap for carbon radicals (2R• + PhSeSePh → 2PhSeR). Much of this parallels the redox chemistry of dioxygen.

Contribution from the Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, Ontario L8S 4M1, Canada

Reactions of S₄N₄ and S₃N₃Cl₃ with Selenium Chlorides. The Preparations and Crystal Structures of SeS₂N₂Cl₂, (S₅N₅)(SeCl₅), and the Disordered Materials (SeₓS₃₋ₓN₂Cl)(SbCl₆)

Ronald J. Gillespie,* James P. Kent, and Jeffery F. Sawyer

The reactions of S₄N₄ with SeCl₄ and of S₃N₃Cl₃ with Se₂Cl₂ in 1:1 molar ratios in SO₂ as solvent give the crystalline compounds (S₅N₅)(SeCl₅) (1) and SeS₂N₂Cl₂ (2), respectively. Compound 2 is also obtained by the reaction of 2 mol of S₃N₃Cl₃ with 3 mol of Se₂Cl₂ in acetonitrile. Orange crystals of 1 are orthorhombic, space group *Pnma*, with *a* = 11.252 (2) Å, *b* = 12.075 (2) Å, *c* = 9.987 (2) Å, *V* = 1356.4 (4) Å³, and *D_c* = 2.38 g cm⁻³ for *Z* = 4. Red-orange crystals of 2 are monoclinic, space group *P2₁/c*, with *a* = 10.447 (2) Å, *b* = 9.259 (2) Å, *c* = 13.529 (3) Å, *β* = 105.93 (2)°, *V* = 1258.4 (4) Å³, and *D_c* = 2.55 g cm⁻³ for *Z* = 4 (ion pair + molecule). In 1 the pentathiazyl S₅N₅⁺ cation and square-pyramidal SeCl₅⁻ anion have crystallographic mirror symmetry and are strongly associated by a short Se–N contact of length 2.794 (5) Å in the sixth coordination site around the selenium. Compound 2 surprisingly contains both a neutral molecule SeS₂N₂Cl₂ and an intimate ion pair SeS₂N₂Cl⁺Cl⁻ in the same lattice. In the neutral molecule the Se atom has an AX₄E disphenoidal primary geometry and an overall AX₄Y′₂E distorted-octahedral geometry while the geometry of the Se atom in the ion pair is AX₃Y₃E distorted octahedral. The Se⋯Cl secondary contacts in this structure are described and discussed. The ¹⁵N NMR spectrum of 2 in 100% sulfuric acid has a pair of doublets at δ = −51.7 and −137.8 ppm with *J*₁₅ₙ₋₁₅ₙ = 5.6 Hz while the ⁷⁷Se NMR spectra of natural-abundance and ¹⁵N-enriched SeS₂N₂Cl₂ have a singlet and a doublet with *J*₇₇Se₋₁₅ₙ = 117.8 Hz, respectively, at δ = 326.0 ppm consistent with the formation of the SeS₂N₂Cl⁺ cation in solution. Further reactions of S₄N₄ with Se₂Cl₂/SbCl₅ or SeCl₄/SbCl₅ mixtures in SO₂ gave disordered compounds with the general formula SeₓS₃₋ₓN₂Cl⁺SbCl₆⁻ (*x* = 0–3). Some crystallographic data for these compounds are reported.

Introduction

Recently, we reported the characterization of the dimeric thiodiselenazyl cation Se₄S₂N₄²⁺ in the compounds (Se₄S₂N₄)(MF₆)₂ (M = As, Sb).[1] Previous workers have reported species

that may contain similar or related ring systems from the reactions of S₄N₄, S₃N₃Cl₃, or bis[bis(trimethylsilyl)amino]sulfane with selenium halides,[2-7] although none of the products of these re-

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