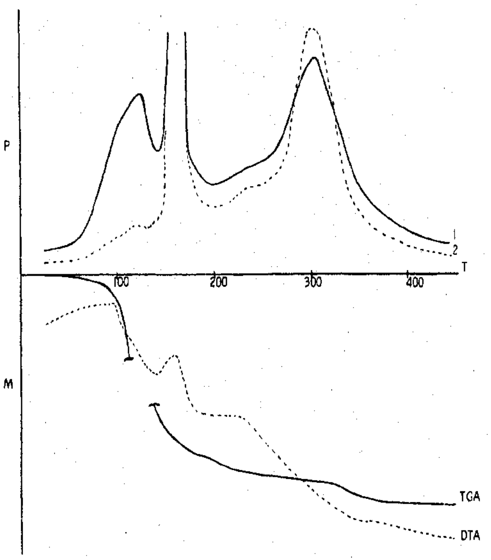

Figure 1. Vacuum DTA–TGA of $H_4AlMgBH_4$: (1, —) change in pressure, (2, ---) pressure change after liquid nitrogen trap.

the second decomposition is exothermic followed by an endothermic effect, and the third decomposition is a broad endotherm. The first gas evolution is attributed to the evolution of solvated THF. The second decomposition at 165 °C, accompanied by noncondensable gas evolution, can be attributed to decomposition of AlH_4MgBH_4 to $BH_3{\cdot}AlH_3$ and MgH_2 with simultaneous decomposition of $BH_3{\cdot}AlH_3$ to give H_2. The last endotherm is due to the decomposition of MgH_2. The steps involved in the decomposition are shown below. No

$$\text{step 1:}\quad AlH_4MgBH_4{\cdot}2THF \rightarrow AlH_4MgBH_4 + 2THF \tag{13}$$

$$\text{step 2:}\quad AlH_4MgBH_4 \rightarrow Al{\cdot}B + MgH_2 + 3H_2 \tag{14}$$

$$\text{step 3:}\quad MgH_2 \rightarrow Mg + H_2 \tag{15}$$

THF cleavage was observed during the thermal decomposition process.

Registry No. $HMgAlH_4$, 12693-01-5; HMgCl, 22106-77-0; NaCl, 7647-14-5; $HMgBH_4$, 12693-03-7; $ClMgBH_4$, 62816-03-9; AlH_4MgBH_4, 62881-85-0; AlH_3, 7784-21-6; MgH_2, 7693-27-8; $NaAlH_4$, 13770-96-2; $Mg(AlH_4)_2{\cdot}4THF$, 25610-40-6; $NaBH_4$, 16940-66-2; $Mg(BH_4)_2$, 16903-37-0; diborane, 19287-45-7; $BH_3{\cdot}THF$, 14044-65-6.

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S_4: An ab Initio Study

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The relative stability of ten possible electronic and conformational states of S_4 has been studied by ab initio STO-3G and 44-31G calculations. The STO-3G optimized geometry is significantly different from the 44-31G optimized geometry and the standard routine to carry out single 4-31G calculations at STO-3G optimized geometries is not appropriate here. Based on the present study in conjunction with previous experimental and theoretical enthalpies of formation for S_4, the triplet helix diradical is predicted to be the most stable among all possible forms including the *c*-S_4. The branched molecule, sulfur trithiotrioxide (trigonal S_4), which has been proposed by extended Hückel calculations, seems unlikely to exist according to the present study. The validity of the use of molecular total overlap population to explain the order of relative stability is also examined.

Elemental sulfur,[1,2] which has been known and used for several thousand years, can exist in a polymeric form and as a variety of rings containing different numbers of sulfur atoms. Many of them have been isolated and structurally elucidated. However, the structure of S_4 remains an interesting unsolved problem.[1,2]

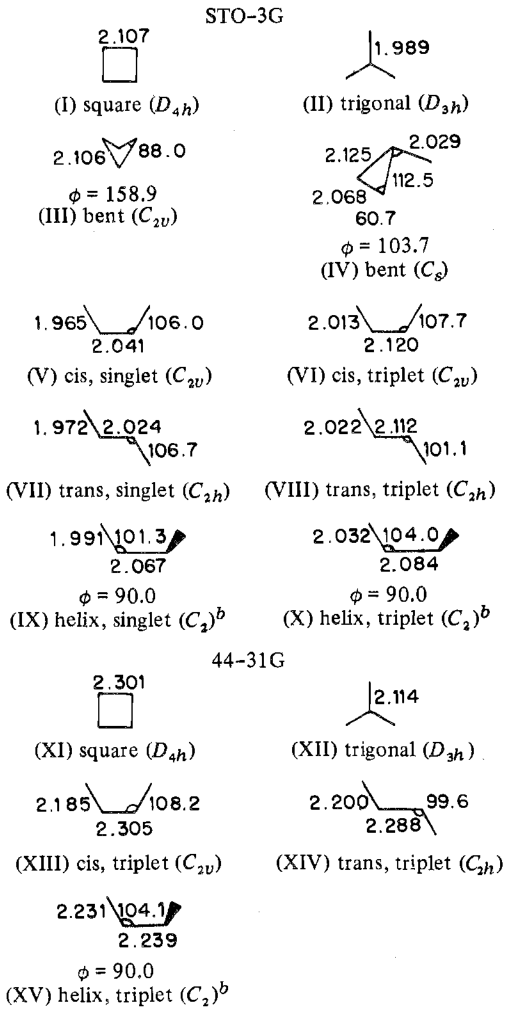
The S_4 molecule is known to exist in the gas and the liquid phase. Several possible structures have been proposed including a ring, a diradical, a bipolar compound, or a chain with double bonds. But, none of these has been experimentally determined. Recent extended Hückel calculations,[1,3] based on spectroscopic atomic parameters, gave a special stability to a branched structure, sulfur trithiotrioxide. Our molecular mechanics calculations[4] suggest that the existence of *cyclo*-tetrasulfur as the most stable structure is unlikely since it is highly strained with a steric energy almost 10 times that found in *cyclo*-hexasulfur and an S–S bond energy about 12 kcal/mol smaller than the corresponding value for *cyclo*-hexasulfur. However, thermodynamic[5] and photoionization[6] data seem to favor the ring although they are insufficient to determine the structure of S_4.[1] It seems to us that there is no unique answer so far about the most stable structure of the S_4 molecule.

An alternative way to attack this problem is ab initio molecular orbital theory which has been described in detail elsewhere.[7] In this paper, ab initio molecular orbital theory is employed to study the structures and stabilities of ten possible electronic and conformational states of S_4.

Computational Aspects and Results

The results presented here were obtained using the Gaussian 70 system of programs.[8,9] The linear-chain, branched-chain, branched-ring, and single-ring forms were all examined at the STO-3G level since its small size permits full optimization under reasonable cost for a molecule as large as S_4. This

Table I. Equilibrium Geometries (Å or deg) and Symmetries[a]



STO-3G

(I) square (D_{4h})

(II) trigonal (D_{3h})

$\phi = 158.9$
(III) bent (C_{2v})

$\phi = 103.7$
(IV) bent (C_s)

(V) cis, singlet (C_{2v})

(VI) cis, triplet (C_{2v})

(VII) trans, singlet (C_{2h})

(VIII) trans, triplet (C_{2h})

$\phi = 90.0$
(IX) helix, singlet (C_2)[b]

$\phi = 90.0$
(X) helix, triplet (C_2)[b]

44-31G

(XI) square (D_{4h})

(XII) trigonal (D_{3h})

(XIII) cis, triplet (C_{2v})

(XIV) trans, triplet (C_{2h})

$\phi = 90.0$
(XV) helix, triplet (C_2)[b]

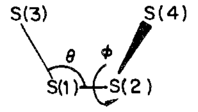
[a] ϕ is the conventional dihedral angle. [b] Presumably, the point symmetry was erroneously assigned as "no sym, C_s" in ref 1.

Table II. Total and Relative Energies

Molecular geometry	STO-3G energy, hartrees	Rel energy, kcal/mol	44-31G energy, hartrees	Rel energy, kcal/mol
I	−1572.682 69	1.27	−1588.130 54	54.71
II	−1572.496 96	117.82	−1588.067 27	94.41
III	−1572.684 22	0.31	−1588.134 37	52.30
IV	−1572.585 29	62.39	−1588.092 55	78.54
V	−1572.559 23	78.75	−1588.093 35	78.04
VI	−1572.676 91	4.90	*a*	
VII	−1572.544 81	87.79	−1588.079 50	86.73
VIII	−1572.680 38	2.72	*a*	
IX	−1572.521 20	102.61	−1588.058 20	100.10
X	−1572.684 72	0	*a*	
XI			−1588.179 53	23.96
XII			−1588.083 35	84.32
XIII			−1588.210 77	4.36
XIV			−1588.213 47	2.67
XV			−1588.217 72	0

[a] Resulted in a different electronic configuration; see text.

method has proven useful in structural studies of dimethyl disulfide,[10] methyl ethyl disulfide,[11] *cyclo*-hexasulfur,[4] *cyclo*-octasulfur,[12] and numerous other molecules including divalent dicoordinate sulfur compounds.[7,13,14] The minimal basis set is expected to give fairly reliable structural predictions without augmenting it with *d* functions for several kinds of compounds.[12-16] A single calculation at the extended 44-31G level using the STO-3G optimized geometry was then carried out in order to assess relative molecular energetics more accurately as suggested by previous experience in compounds involving only first-row atoms.[17] However, several structures of S_4 (Table I) were also optimized at the 44-31G level since it was found later that the STO-3G optimized geometries are rather different from those obtained at the 44-31G level (vide infra). Open-shell triplet states were calculated by the unrestricted Hartree–Fock method of Pople and Nesbet.[18] Each structure is fully geometrically optimized subject only to an overall symmetry constraint with the exception that the dihedral angle ϕ (1) of the helix chain was assumed to be 90°.



I

Calculated equilibrium geometries and energies (total and relative) for the corresponding electronic and conformational states are listed respectively in Tables I and II.

Discussion

As can be seen from Table I, there is a surprisingly large difference (about 0.2 Å) in the equilibrium bond lengths calculated using the STO-3G and 44-31G basis sets although bond angles agree quite well each other. The results presented here are consistent with the recent observation[14] that the addition of a full set of valence orbitals to a minimal basis tends to increase bond lengths. The S–S bond lengths obtained by the STO-3G method are expected to be rather close to experimental values.[10,13] But, one should note that although the absolute errors for 44-31G bond lengths are generally large, the calculated bond lengths are expected to be long consistently.[14]

It has been shown[19] that ab initio calculations at the STO-3G level are not at all satisfactory for energetic comparisons between wholly acyclic molecules and those containing small rings. The usual practice is to carry out 4-31G or even higher level calculations at the STO-3G optimized geometries. Similar phenomena are expected here and one may pursue energetic comparisons according to the standard procedure. However, the standard procedure is not appropriate here because the STO-3G geometries are very much different from the 44-31G geometries. Indeed, single 44-31G calculations at the STO-3G optimized geometries of open-shell *trans*-, *cis*-, and *helix*-S_4 lead to wrong configurations. It should also be noted that even the extended 4-31G (and hence 44-31G) level may not be entirely satisfactory for *accurate* energetic comparisons and the inclusion of polarization-type functions in the basis has been suggested.[19,20] Another problem related to the present study is the uncertainty of the energetic comparison between triplet and singlet states since single-determinant theory is known to favor triplet states unduly. By how much the triplet is unduly preferred for the system studied here is totally unknown. However, it is possible that qualitatively correct results may be obtained at the 44-31G level of theory and in case of ambiguity the available experimental and theoretical data may be able to clarify it.

The calculated electronic configurations for triplet-chain forms are as follows: $(4a_u)^1(4b_g)^1$ for *trans*-S_4; $(4b_1)^1(4a_2)^1$ for *cis*-S_4; $(16b_1)^1(17a_1)^1$ for *helix*-S_4. To check whether these obtained configurations correspond to the lowest energy arrangements, several other configurations were examined. All of them result in an increase in energy and rather different equilibrium geometry. For instance, the *trans*-S_4 with configuration $(13a_g)^1(4b_g)^1$ is 68 kcal mol^{-1} higher in energy than the $(4a_u)^1(4b_g)^1$ *trans*-S_4 and has different equilibrium geometry; S(1)–S(2) = 2.328 Å, S(1)–S(3) = 1.963 Å, and θ = 106.9°.

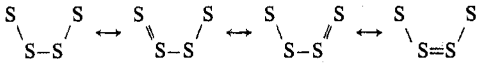
Table III. Overlap Populations for Possible Conformations and Electronic States at Their Energy Minima[a,b]

Molecular geometry	Nearest		Next nearest		Second next nearest		Total	
	STO-3G	44-31G	STO-3G	44-31G	STO-3G	44--31G	STO-3G	44-31G
I	157 (4)	91 (4)	−16 (2)	−78 (2)			597	206
II	160 (3)	57 (3)	−8 (3)	−42 (3)			456	47
III	159 (4)	95 (4)	−21 (2)	−97 (2)			593	184
IV	133 (2) 112 (1) 137 (1)	−8 (2) 23 (1) 56 (1)	−7 (2)	−34 (2)			500	−3
V	201 (2) 164 (1)	146 (2) −5 (1)	−18 (2)	−87 (2)	3 (1)	21 (1)	534	133
VI	184 (2) 146 (1)		−9 (2)		−1 (1)		495	
VII	191 (2) 174 (1)	91 (2) 40 (1)	−14 (2)	−53 (2)	0 (1)	1 (1)	528	116
VIII	183 (2) 151 (1)		−10 (2)		0 (1)		497	
IX	188 (2) 163 (1)	87 (2) 80 (1)	−16 (2)	−74 (2)	1 (1)	12 (1)	508	118
X	178 (2) 163 (1)		−12 (2)		0 (1)		519	
XI		146 (4)		−37 (2)				510
XII		107 (3)		−23 (3)				252
XIII		165 (2) 117 (1)		−21 (2)		3 (1)		408
XIV		155 (2) 124 (1)		−22 (2)		0 (1)		390
XV		145 (2) 143 (1)		−28 (2)		1 (1)		378

[a] All values should be multiplied by 10^{-3}. [b] The digits appearing in parentheses represent the number of associated type of interactions.

The triplet states of chain forms—cis, trans, and helix—are predicted to be lower in energy than their corresponding closed-shell singlets by at least 75 kcal mol^{-1}. Because of the large energy splitting it seems impossible that the singlet chain would be lower in energy in reality, although single-determinant theory is known to favor states of high-spin multiplicity. However, if molecular orbitals are allowed to become complex,[21] the singlet–triplet (both being now open shell) energy difference may become much less.

The calculated terminal bonds in singlet-chain forms are extremely short as compared with theoretical bond lengths found in sulfanes and polysulfides.[10,13] The calculated STO-3G charge densities show that the terminal S atoms are negatively charged (for example, −0.08 e for *cis*-S_4) and the central S atoms are correspondingly positively charged. The dipole direction is hence pointed from the midpoint of the central S–S bond to the midpoint of the S(3)···S(4) line. The predicted dipole moments for singlet *cis*-S_4 and *helix*-S_4 forms are respectively 1.65 and 0.93 D. Both calculated bond lengths and charge densities seem to suggest that structures **3**–**5** are

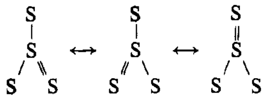


2 3 4 5

important in determining the equilibrium geometry for the singlet S_4 chain. The existence of 2-butene- and 1-butene-like structures may explain partially why the *cis*- and *trans*-S_4 conformations are more stable than the *helix*-S_4 for the singlet S_4 chain.

For triplet states, structures **3**–**5** are unlikely due to possible spin–spin interactions. Indeed, calculated bond lengths for triplet-chain forms are longer than their corresponding bonds in singlet forms. The calculated dipole moments for *cis*- and *helix*-S_4 are respectively 0.58 and 0.29 D for STO-3G and 0.95 and 0.44 D for 44-31G, which are not only smaller in magnitude than their singlet counterparts but also opposite in direction. The helix form with the 90° dihedral angle being assumed is calculated to be the most stable conformation for the triplet chain. The stability of the helix form and the predicted dipole direction show the lack of importance of structures **3**–**5** for the triplet chain. The calculated cis and trans barriers, about 5 and 3 kcal mol^{-1}, respectively, are not much difference from their theoretical (STO-3G) counterparts in R–S–S–R.[10] One also notes that higher barrier heights (11 and 7 kcal mol^{-1}) have been suggested.[4,10,22]

The trigonal form, which was once assumed to be the most stable due to its structural resemblance to SO_3 is, surprisingly, the least stable among all forms in Table I, although both the charge distribution (+0.22 e on the central S for STO-3G and +0.07 e for 44-31G) and the rather short bond length (1.989 and 2.114 Å respectively for STO-3G and 44-31G) still suggest a resonance structure (**6**).



6

On the basis of 44-31G calculations, the planar form of *cyclo*-tetrasulfur is predicted to be 24 kcal mol^{-1} less stable than the triplet helix. The calculated STO-3G bond length, 2.107 Å, is in acceptable agreement with the theoretical value, 2083 Å, obtained from the molecular mechanics calculations[4] and the experimental value,[23] 2.10 Å, found in 1,2-dithiolane-4-carboxylic acid. The much longer S–S bond length (about 0.05 Å longer) than those found in *c*-S_6,[24a] *c*-S_8,[24b–d] and *c*-S_{12}[24e] is expected since the repulsion between the lone-pair electrons in 3pπ AO's on each sulfur of the central S–S bond is maximized when the dihedral angle approaches 0°.

Complete geometrical optimization of *cyclo*-tetrasulfur at the STO-3G level indicates that the overall sulfur skeleton deviates from planarity by 21.1°; this is in contrast to what was obtained by previous molecular mechanics calculations.[4] The calculated barrier to ring inversion is 1.0 kcal mol^{-1} at the STO-3G level. Theoretical values for both the ring-puckering angle and the inversion barrier through a planar ring in *c*-S_4 are somewhat larger than those found in cyclobutane.[19]

The branched-ring form, trithiacyclopropane-1-thione, has also been examined. It is predicted to be more stable than sulfur trithiotrioxide while less stable than ring and chain forms. The predicted dipole moment is 3.16 D at the STO-3G level with the branched S being negatively charged by 0.03 e.

Results presented here indicate that in the gas phase the molecule favors the triplet helix over other forms. One may argue that the energy splitting (about 23 kcal mol^{-1})[26] between the bent c-S_4 and the triplet helix is not large enough to ensure the triplet diradical being the ground state for S_4. One notes that there are two pieces of evidence which suggest that the stability order obtained here is reliable. The one is from the experimentally available absorption band (530 nm) for S_4.[27] It has been suggested that sulfur rings are isovalent to cycloalkanes and are expected to have large energy gaps between the HOMO and the LUMO while the open-chain S_n allotropes are isovalent to alkane diradicals and are expected to be colored.[3] The available absorption band for S_4 thus prefers the diradical to the ring. Indeed, 44-31G calculations predict a large energy gap between the HOMO and the LUMO for c-S_4 (8.78 ev) as well as trigonal S_4 (6.82 ev). The 44-31G results are in contrast to previous predictions based on extended Hückel calculations in which trigonal S_4 was shown to be colored.[3] The second evidence comes from molecular mechanics calculations[4] which give 64 kcal mol^{-1} for the heat of formation for *the S_4 ring.* The molecular mechanics value is much larger than the experimental estimate[28] for *the S_4 molecule.* The only reasonable explanation for the discrepancy seems to be that the experimental estimate corresponds to the value for the diradical while the result obtained from the molecular mechanics method corresponds to the value for the ring. Note also that there is reasonable agreement between the energy difference (23 kcal mol^{-1}) of ring and helix forms obtained by the ab initio procedure and the enthalpy difference (29 kcal mol^{-1}) of the experimental estimate and that calculated by the molecular mechanics method.

Table III lists all overlap populations for possible conformations and electronic states of S_4. As can be seen from Table III, the lack of validity of the standard routine to do single 44-31G calculations at the optimized STO-3G geometries results in the rather absurd Mulliken population analysis. First, the next-nearest (1,2-bonded) interactions are rather small when compared with STO-3G results and are sometimes of antibonding character (negative population). Second, all types of interactions are almost all of the same order no matter whether they are nearest, next nearest (1,3 nonbonded), or second next nearest (1,4 nonbonded). It is of interest to note here that Mulliken population analysis shows that the next nearest interactions are of antibonding nature (repulsive) while the second next-nearest interactions are usually of very weak attraction.

There is a growing tendency to rationalize the order of conformational relative stability in terms of the molecular total overlap population (MTOP), which is the sum of all atom-pair overlap populations in a molecule. It has been assumed that MTOP is a maximum when the total calculated energy reaches a minimum.[29,30] Detailed analysis of Table III reveals that MTOP cannot be employed to describe the conformational preference of c-S_4 although it is useful for the singlet straight chain. However, it should be noted that Mulliken population analysis does correctly indicate the S–S bonding strength in the bent c-S_4 being stronger than that in the square.

Earlier extended Hückel results,[3] based on spectroscopic atomic parameters, might give wrong predictions about the order of stability of different allotropes of S_4 due to its shortcomings. The trouble with most existing empirical or semiempirical methods is that they are usually reliable only as interpolating schemes but are of uncertain validity in extrapolations. One also notes that the fixed geometries assumed in their study are quite different from those optimized by us and it is generally believed that electronic energies are usually quite geometry dependent. On the other hand, the ab initio calculations at STO-3G and 44-31G levels are not infallible either. The use of a larger basis set with inclusion of d-type polarization functions as well as configuration interactions would be desirable. Unfortunately, calculations involving polarization functions and/or configuration interactions are extremely costly in terms of computing time. However, I do feel that results presented here are qualitatively correct due to the well-established reliability of the methods used. It is my hope that this work will stimulate further theoretical and experimental research in this area.

In short, on the basis of ab initio molecular orbital calculations using STO-3G and 44-31G basis sets in conjunction with previous experimental and theoretical works, the triplet helix diradical is predicted to be the most stable structure for the S_4 molecule and the bent c-S_4 the next most stable. The possibility that sulfur forms branched molecules, sulfur trithiotrioxide here, seems highly unlikely according to the present calculations. The use of MTOP to explain conformational preference is not fully warranted.

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Registry No. S_4, 19269-85-3.

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Lower Oxidation States of Selenium. 2. Potentiometric Study Involving Tetravalent Selenium, Tetraselenium (2+), Octaselenium (2+), and Three Other Low Oxidation States of Selenium in a Chloroaluminate Melt

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The solvated entities Se_4^{2+} and Se_8^{2+} have been identified in reaction mixtures of dilute $SeCl_4$ and elementary selenium by a potentiometric method supplemented by a spectrophotometric method. The three other low oxidation states of selenium are believed to be Se_2^{2+}, Se_{12}^{2+}, and Se_{16}^{2+}. The solvent is low-melting NaCl–$AlCl_3$ (37:63 mol %) at 150 °C. p*K* values (based on molar concentrations) are given for the reactions $2Se^{4+}(soln) + 3Se_4^{2+}(soln) \rightleftarrows 7Se_2^{2+}(soln)$ (1), $4Se^{4+}(soln) + 7Se_8^{2+}(soln) \rightleftarrows 15Se_4^{2+}(soln)$ (2), $Se_4^{2+}(soln) + Se_{12}^{2+}(soln) \rightleftarrows 2Se_8^{2+}(soln)$ (3), and $Se_8^{2+}(soln) + Se_{16}^{2+}(soln) \rightleftarrows 2Se_{12}^{2+}(soln)$ (4). For the four equilibria the potentiometric method gave p*K* values of 7.9, −12.5, −2.9, and 0.0 with nonlinear confidence limits (95%) of 4.7 to 9.1, −∞ to −12.4, −∞ to −2.5, and −0.2 to 0.2, respectively. Calculation based on earlier spectrophotometric data at 150 °C for equilibria 3 and 4 gave p*K* values of −2.0 and −0.8 with nonlinear confidence limits (95%) of −∞ to −0.7 and −∞ to +2.4, respectively; no p*K* value was determined for the first reaction and no well-defined p*K* value could be determined for the second reaction; however, the nonlinear confidence limits (95%) could be determined for the second reaction to be −∞ to −5.5.

Introduction

In a previously published paper[1] it was shown that four species were formed by reduction of a solution of $SeCl_4$ in an acidic NaCl–$AlCl_3$ (37:63 mol %) melt with elementary selenium. The two highest oxidation states of these species were found to be $+^1/_2$ and $+^1/_4$ (or possibly $+^4/_{17}$), whereas no accurate value could be calculated for the two lowest oxidation states. As possible formulas for these species Se_4^{2+}, Se_8^{2+}, Se_{12}^{2+}, and Se_{16}^{2+} were proposed. In the present paper good evidence (based on potentiometric measurements) is given for Se_4^{2+} and Se_8^{2+} and the existence of Se_{12}^{2+} and Se_{16}^{2+} is shown to be reasonable. Furthermore the results indicate that there is a fifth low oxidation state of selenium present, probably Se_2^{2+}. The presence of Se_4^{2+} and Se_8^{2+} is in agreement with the results found in sulfuric acid by Gillespie and co-workers.[2] The results obtained by Corbett and co-workers[3] seem to indicate that the same two ions are formed in chloroaluminate melts. The structure of Se_4^{2+} in $Se_4(HS_2O_7)_2$ is square planar[4] and the structure of Se_8^{2+} in $Se_8(AlCl_4)_2$ is bicyclic.[5]

Experimental Section

The chemicals used in the present work were prepared in the same way as in the previous work on selenium.[1] The experimental technique was the same as described in a recent article about the lower oxidation states of tellurium,[6] where an electrochemical cell with inert electrodes of glassy carbon was used for the potentiometric measurements.[7] The furnace used has been described in detail in connection with a method for determination of densities of molten salts.[8] The materials that made up a melt were weighed in a nitrogen-filled glovebox, where the water content was ca. 5 ppm. To avoid decomposition of the $SeCl_4$ used it was kept in small sealed glass tubes until used.

Results and Discussion

Cell Potentials. As demonstrated in a previous publication about low oxidation states of tellurium,[6] an electrode cell made of Pyrex with vitreous carbon fused into the bottom can be used to measure redox potentials of the different tellurium species. The same type of cell can also be used to measure redox potentials of the low oxidation states of selenium.

If we look at one redox pair which we will call Se_q^{r+} and Se_v^{x+} (r, q, v, and x are integers), the composition of the cell can be given as

$$\text{carbon I}\left|\begin{array}{l}\text{solution I}\\ \mathrm{Se}_q^{r+}\text{ and }\mathrm{Se}_v^{x+}\\ \text{in NaCl–AlCl}_3\\ (37{:}63\text{ mol }\%)\end{array}\right|\text{porous pin}\left|\begin{array}{l}\text{solution II}\\ \mathrm{Se}_q^{r+}\text{ and }\mathrm{Se}_v^{x+}\\ \text{in NaCl–AlCl}_3\\ (37{:}63\text{ mol }\%)\end{array}\right|\text{carbon II} \qquad (1)$$

At each electrode we have the equilibrium

$$q\mathrm{Se}_v^{x+} \rightleftarrows v\mathrm{Se}_q^{r+} + n\mathrm{e}^- \qquad (2)$$

where e^- is the electron and n is the number of electrons. Analogous to the calculation performed on the tellurium system[6] it can be shown that the potential of the concentration cell is given by

$$\Delta E = \frac{RT}{F}\ln\frac{[\mathrm{Se}_q^{r+}]_{\mathrm{II}}^{v/n}[\mathrm{Se}_v^{x+}]_{\mathrm{I}}^{q/n}}{[\mathrm{Se}_q^{r+}]_{\mathrm{I}}^{v/n}[\mathrm{Se}_v^{x+}]_{\mathrm{II}}^{q/n}} \qquad (3)$$

where R, T, and F have their usual meaning. The variation in the activity coefficients has been neglected in the present work. This is based on the same arguments as given in the recent article dealing with the tellurium system.[6]

A plot of the measured ΔE vs. the Se:$SeCl_4$ formality ratio (designated R) is given in Figure 1. The formality is defined as the initial molar amount of any of the added substances dissolved in 1 L of the melt. The plot in Figure 1 shows some of the same features as the spectrophotometric plot for the same system in the same R range.[1] It is for example clear that there must be a sharp change in concentrations of the species around a formality ratio of 15. It is furthermore important to notice that there is no change in ΔE after a formality ratio of ca. 31 is reached; this must mean that the melt is saturated above this formality ratio.

As in the work on the low oxidation states of tellurium[6] the compositions in the two cell compartments were increased alternately, while interchanging the compartments used for measurement and reference. A small difference in composition