

# Notes

## Chalcogenospecific Synthesis of 1,2-Se<sub>2</sub>S<sub>6</sub> Using ZnS<sub>6</sub>(TMEDA)

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### Introduction

The compound (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiS<sub>5</sub> has allowed the rational syntheses of many sulfur homo- and heterocycles.<sup>1</sup> This reagent serves as a reliable source of the S<sub>5</sub><sup>2-</sup> unit, thereby defining a route to cyclic compounds of the type cyclo-S<sub>5+x</sub> and related Se–S rings.<sup>2</sup> The coproducts and starting reagents are fairly chemically inert thus minimizing nucleophile-induced rearrangements of unstable cyclic polysulfanes. Starting in the early 1980s, we reported a second generation of polychalcogen group transfer reagents based on titanocene complexes with altered polychalcogenide ligands. Representative species include 1,4-[(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiE<sub>2</sub>]<sub>2</sub> (E = S,<sup>3</sup> Se<sup>4</sup>), 1,5-[(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiS<sub>3</sub>]<sub>2</sub>,<sup>5</sup> (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiS<sub>2</sub>SiMe<sub>2</sub>,<sup>6</sup> (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiS<sub>2</sub>PSAr,<sup>7</sup> and (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiS<sub>4</sub>CR<sub>2</sub>.<sup>8</sup> Steudel and co-workers have made extensive use of these and related organotitanium reagents for the preparation of many novel heterocyclic compounds.<sup>9</sup>

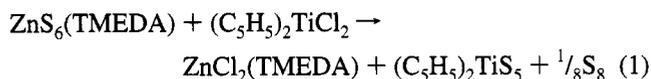
Given the successes seen for titanocene compounds it is interesting to consider the development of reagents based on other metals which might, for example, deliver different types of polychalcogen groups. The present report describes the use of such a reagent that is noteworthy since (i) it is based on zinc, not titanium, (ii) it is very easily prepared, and (iii) it delivers S<sub>6</sub><sup>2-</sup>, a fragment not previously available.

### Results and Discussion

**Basic Properties of ZnS<sub>6</sub>L<sub>2</sub>.** We have recently reported the syntheses of a variety of compounds of the type ZnS<sub>6</sub>L<sub>2</sub> where L is a nitrogenous base.<sup>10</sup> One derivative of particular interest is ZnS<sub>6</sub>(TMEDA) (TMEDA = N,N,N',N'-tetramethylethylene-

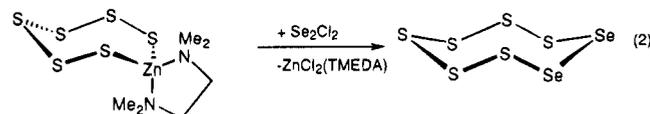
diamine). This highly soluble species can be prepared directly from the reaction of sulfur with a suspension of zinc in hot TMEDA.

**Polysulfide Transfer Strength of ZnS<sub>6</sub>L<sub>2</sub>.** We were initially interested in establishing the relative S<sub>x</sub> transfer strength of the zinc polysulfide reagent relative to the well known titanocene polychalcogenide reagents. This point was demonstrated with the reaction depicted in eq 1. This transformation proceeds very



cleanly, requiring only a few hours at room temperature. It is obvious from the equation that the zinc reagent could have been expected to generate (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiS<sub>6</sub>.<sup>11</sup> When we monitored the reaction by <sup>1</sup>H NMR spectroscopy (CD<sub>2</sub>Cl<sub>2</sub> solution), the only observed product was the known pentasulfido complex. The Zn to Ti transfer reaction does generate small amounts of side products characterized by minor signals in the C<sub>5</sub>H<sub>5</sub> region of the <sup>1</sup>H NMR spectra which conceivably result from decomposition of an unstable hexasulfido species. If (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiS<sub>6</sub> indeed forms, its rate of decomposition is faster than its rate of formation.

**Preparation of 1,2-Se<sub>2</sub>S<sub>6</sub>.** The utility of the zinc reagent as a precursor to hexasulfido compounds was demonstrated via its reaction with Se<sub>2</sub>Cl<sub>2</sub>. The reaction was conducted by treating a CS<sub>2</sub> slurry of ZnS<sub>6</sub>(TMEDA) with neat Se<sub>2</sub>Cl<sub>2</sub> at –60 °C (eq 2). The reaction mixture quickly changed from yellow to red-



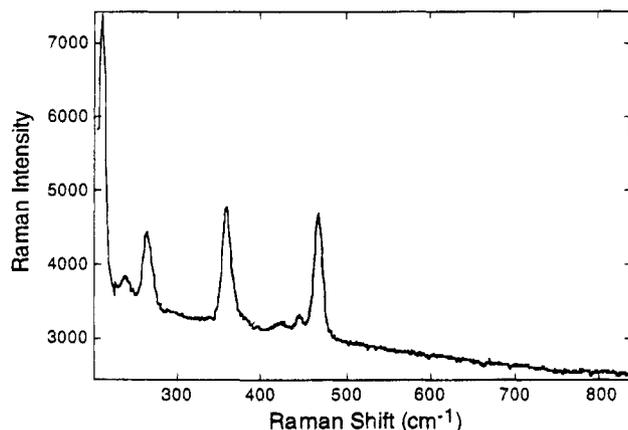
orange and after a short time it was filtered to remove the spent zinc reagent. After recrystallization, we obtained a 62% yield of analytically pure Se<sub>2</sub>S<sub>6</sub> as orange-yellow crystals. HPLC analysis on a reverse phase column showed a single peak with a retention time similar to that of sulfur.

The <sup>77</sup>Se NMR spectrum of the new compound showed a single resonance at 631 ppm. Previous work by Steudel and Laitinen on S<sub>x</sub>Se<sub>y</sub> mixtures had assigned this chemical shift to 1,2-Se<sub>2</sub>S<sub>6</sub>.<sup>12</sup> In the crown conformation, 1,2-Se<sub>2</sub>S<sub>6</sub> features equivalent Se atoms which are related via a C<sub>2</sub> rotation axis. The <sup>77</sup>Se chemical shifts of an Se atom flanked by one atom each of Se and S occur in the range of 690–620 ppm.<sup>2</sup>

The IR spectrum of 1,2-Se<sub>2</sub>S<sub>6</sub> shows ν<sub>ss</sub> at 458 cm<sup>-1</sup> as compared to 469 cm<sup>-1</sup> observed for S<sub>8</sub>. The Raman spectrum consists of distinct peaks for Se–Se, Se–S and S–S vibrations at 263, 360 and 464 cm<sup>-1</sup> respectively (Figure 1). The coupling between the two Se–S vibrations is normally not detectable in compounds with S–Se–Se–S linkages.<sup>13a</sup> A strong peak at 202 cm<sup>-1</sup> can be attributed to δ<sub>sss</sub> of the ring. On the basis of the absence of any peak at ~ 218 cm<sup>-1</sup>, we have concluded

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**Figure 1.** Raman spectrum of solid 1,2-Se<sub>2</sub>S<sub>6</sub> ( $\lambda_{\text{excit}} = 647.1 \text{ nm}$ ).

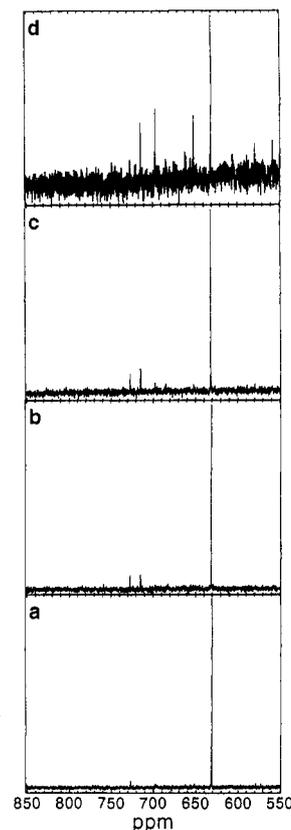
that the sample is free of S<sub>8</sub>,<sup>13b</sup> which could not be confirmed unambiguously by HPLC or <sup>77</sup>Se NMR measurements.

**Physical Properties of 1,2-Se<sub>2</sub>S<sub>6</sub>.** The orange-yellow solid was obtained as monoclinic crystals. Attempts are continuing to obtain a reflection data set of sufficient quality to allow refinement of the atomic structure.<sup>14</sup> Eight membered rings with the average composition Se<sub>2</sub>S<sub>6</sub> crystallize in the space group *P2/c*.<sup>15</sup> It is interesting that the monoclinic phase of S<sub>8</sub> is stable only above 95.4 °C.<sup>16</sup>

1,2-Se<sub>2</sub>S<sub>6</sub> melts sharply at 114.5 °C, 5° less than S<sub>8</sub>. Samples of average composition Se<sub>2</sub>S<sub>6</sub> are reported to melt over the range 107–117 °C.<sup>17a</sup> Differential scanning calorimetric measurements revealed no phase transitions up to the melting point. The heat of fusion ( $\Delta H_f$ ) of  $17.5 \pm 0.8 \text{ kJ/mol}$  was determined by integrating the endothermic transition (111.9–115 °C). For monoclinic sulfur  $\Delta H_f$  is reported to be  $12.8 \pm 1.0 \text{ kJ/mol}$  (mp 119.6 °C),<sup>17b,18</sup> while for samples of average composition Se<sub>2</sub>S<sub>6</sub>, it is reported to be  $10.2 \pm 0.8 \text{ kJ/mol}^{-1}$ .<sup>17a</sup>

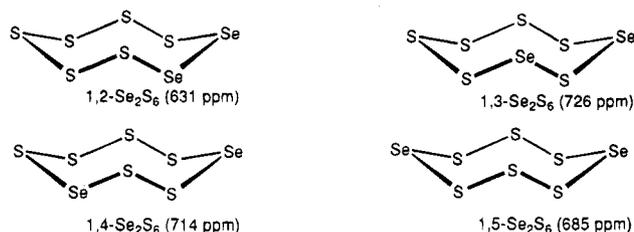
<sup>77</sup>Se NMR measurements show that CS<sub>2</sub> solutions of 1,2-Se<sub>2</sub>S<sub>6</sub> are very stable thermally, as predicted.<sup>19</sup> The <sup>77</sup>Se NMR spectrum of the CS<sub>2</sub> extract of a sample that had been melted and then quickly recooled, showed unchanged 1,2-Se<sub>2</sub>S<sub>6</sub>. CS<sub>2</sub> solutions of this heterocycle show the formation of ~5% 1,3-Se<sub>2</sub>S<sub>6</sub>; the spectrum remains essentially unchanged after 130 h at 40–45 °C. Solutions are stable to air and ambient light for several weeks.

**Rearrangement Reactions of 1,2-Se<sub>2</sub>S<sub>6</sub>.** Solutions of 1,2-Se<sub>2</sub>S<sub>6</sub> are mildly reactive upon UV photolysis. CS<sub>2</sub> solutions of the compound were subjected to photolysis until ~15% conversion. The first product (726 ppm) is 1,3-Se<sub>2</sub>S<sub>6</sub>. Further irradiation gives rise to a peak at 714 ppm which we attribute to 1,4-Se<sub>2</sub>S<sub>6</sub>. Subsequently we observe SeS<sub>7</sub> (697 ppm) and later both 1,5-Se<sub>2</sub>S<sub>6</sub> (685 ppm) and 1,2,3-Se<sub>3</sub>S<sub>5</sub> (651, 558 ppm). These results indicate that photolysis primarily induces an intramolecular rearrangement, otherwise we would expect greater amounts of other Se<sub>x</sub>S<sub>8-x</sub> rings where  $x \neq 2$ . Interpretation of these data relies on the work by Laitinen and co-workers on the <sup>77</sup>Se chemical shifts in Se<sub>x</sub>S<sub>y</sub>.<sup>20</sup> We have reversed their



**Figure 2.** 57 MHz <sup>77</sup>Se NMR spectrum of a CS<sub>2</sub> solution of 1,2-Se<sub>2</sub>S<sub>6</sub> before (spectrum a) and after UV photolysis for 60 (b), 105 (c), and 1140 min (d).

assignments for the 1,4- and 1,5- isomers based on the order of appearance of <sup>77</sup>Se NMR peaks in this photolysis experiment.



## Conclusions

We have demonstrated the utility of ZnS<sub>6</sub>(TMEDA) to transfer S<sub>6</sub><sup>2-</sup> as an intact unit through the synthesis of 1,2-Se<sub>2</sub>S<sub>6</sub>, a species previously available only as a mixture. 1,2-Se<sub>2</sub>S<sub>6</sub> is a rare example of easily prepared stable sulfur selenide available in isomeric purity. This species is of further interest since it allows one to probe isomerism in eight-membered rings by monitoring the relative positions of the two Se atoms. On the basis of our findings, photolysis of 1,2-Se<sub>2</sub>S<sub>6</sub> primarily induces intramolecular rearrangements which could be explained by the transient formation of rings with exocyclic chalcogen atoms.

## Experimental Section

Details of the procedure for the synthesis of ZnS<sub>6</sub>(TMEDA) may be found in a recent paper.<sup>10</sup> Se<sub>2</sub>Cl<sub>2</sub> was used as purchased from Aldrich. CS<sub>2</sub> (Fisher) was degassed before use. Hexane was freshly distilled over CaH<sub>2</sub> under nitrogen.

HPLC experiments were performed in the reverse phase mode with a C18, 5  $\mu$  column (Varian Micropac MCH-5; 4 mm  $\times$  15 cm) with a Varian 2510 pump and a Varian 2550 variable wavelength detector operating at 254 nm. Samples were injected as CS<sub>2</sub> solutions and eluted

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with methanol (1 mL/min). Microanalyses and DSC were performed by the School of Chemical Sciences Microanalytical Laboratory.

$^{77}\text{Se}$  NMR spectra were recorded at 57.34 MHz on a GE 300 NB instrument. The spectra were recorded on  $\text{CS}_2$  solutions, using  $\text{D}_2\text{O}$  or  $\text{C}_6\text{D}_6$  as the lock solvents (in concentric sealed tubes). The  $^{77}\text{Se}$  NMR chemical shifts are reported downfield (ppm) with respect to  $\text{Me}_2\text{Se}$  (neat) as an external standard (0 ppm). The scans were acquired with a delay time of 12 s and 15  $\mu\text{s}$  pulse width. The probe temperature was maintained at  $19.8 \pm 2$  °C.

**Reaction of  $\text{ZnS}_6(\text{TMEDA})$  with  $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ .** A slurry of 0.192 g of  $\text{ZnS}_6(\text{TMEDA})$  (0.5 mmol) and 0.126 g of  $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$  (0.5 mmol) in 18 mL of  $\text{Me}_2\text{CO}$  was stirred for 20 h. The resulting red mixture was filtered, and the filtrate was evaporated. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and chromatographed on silica gel eluting with  $\text{CH}_2\text{Cl}_2$ . The microcrystalline product was identified as pure  $(\text{C}_5\text{H}_5)_2\text{TiS}_5$  by  $^1\text{H}$  NMR spectroscopy.

In a separate experiment, a solution of 0.027 g of  $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$  (0.0108 mmol) in 0.5 mL of  $\text{CD}_2\text{Cl}_2$  was added to a solution of 0.0042 g (0.0112 mmol) of  $\text{ZnS}_6(\text{TMEDA})$  in 0.5 mL of  $\text{CD}_2\text{Cl}_2$ . An integration standard of 0.0025 g of  $\text{Ph}_3\text{CH}$  was added and  $^1\text{H}$  NMR spectra were recorded hourly. The half-life of the reaction was  $\sim 2$  h and the yield of  $(\text{C}_5\text{H}_5)_2\text{TiS}_5$  was  $\sim 80\%$ .

**1,2- $\text{Se}_2\text{S}_6$ .** To a cooled ( $-60$  °C) slurry of 1.217 g (3.25 mmol) of  $\text{ZnS}_6(\text{TMEDA})$  in 30 mL of degassed  $\text{CS}_2$ , 272  $\mu\text{L}$  (3.25 mmol) of neat  $\text{Se}_2\text{Cl}_2$  was added dropwise with stirring. The reaction mixture immediately changed its color to orange-red. It was allowed to warm up to  $-10$  °C over 2 h and then filtered in air. The residue was washed with  $3 \times 10$  mL portions of  $\text{CS}_2$ . The filtrates were combined, diluted with 100 mL of hexanes. The solution was cooled at  $-25$  °C for a few hours, and filtered cold to remove a small amount of dark red solid. The filtrate was evaporated to dryness and the residue was extracted into  $\sim 10$  mL of  $\text{CS}_2$  which was diluted with  $\sim 100$  mL of

hexanes and cooled to  $-30$  °C. The resulting orange-yellow microcrystalline solid was filtered cold, washed with 10 mL of hexane, and dried under vacuum. Yield: 0.702 g (62%). Anal. Calcd for  $\text{Se}_2\text{S}_6$ : S, 54.92; Se, 45.08; Found: S, 54.74; Se, 45.04.  $^{77}\text{Se}$  NMR ( $\text{CS}_2$  solution): 631 ppm (s), downfield of neat  $\text{Me}_2\text{Se}$  (as an external standard). Reverse phase HPLC experiments revealed only one peak with a retention time of 7.14 min.

**Stability Studies.** The thermal stability of 1,2- $\text{Se}_2\text{S}_6$  was tested using a solution of 0.103 g of 1,2- $\text{Se}_2\text{S}_6$  dissolved in 3 mL of  $\text{CS}_2$ . This solution was sealed in a 10 mm NMR tube and heated in an oil bath for 128 h (42–45 °C). We observed  $\sim 5\%$  of 1,3- $\text{Se}_2\text{S}_6$  in the final spectrum (726 ppm).

The photochemical stability of 1,2- $\text{Se}_2\text{S}_6$  was tested using a solution of 0.104 g in 3 mL of  $\text{CS}_2$ . This solution was flame sealed in a 10 mm NMR tube. The tube was immersed in a quartz-jacketed ice bath while being irradiated with a high pressure Hg arc lamp ( $\lambda = 365$  nm) using a Model BM-100 apparatus from Spectronics Corp. The results are shown in Figure 2.

**X-ray Crystallography.** Data were collected on an Enraf Nonius CAD-4 diffractometer using  $\text{Mo K}\alpha$  radiation. A set of 25 standard reflections indicated a monoclinic cell  $a = 8.404(3)$ ,  $b = 13.190(8)$ ,  $c = 9.199(6)$  Å,  $\beta = 123.91^\circ$ . A total of 1243 reflections were collected over the range  $19.2 \leq 2\theta \leq 23.8^\circ$ . Of these, 1019 reflections were  $> 4\sigma$  and were considered in subsequent calculations. Systematic absences suggested the space group  $Pc$  or  $P2/c$ .

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