J. Am. Chem. Soc. **1998,** *120,* 10027−10031

# Synthesis and Unique Properties of 4,8-Bis[bis(diethylamino)methylene]-1,2,3,5,6,7-hexaselenacyclooctane

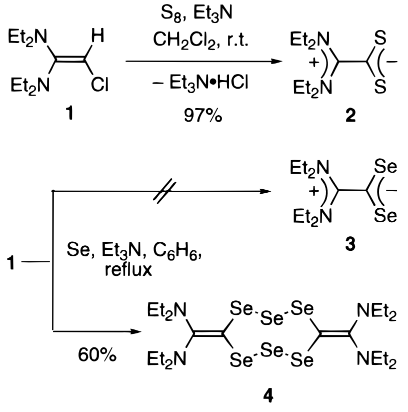
**Juzo Nakayama,*,† Isao Akiyama,† Yoshiaki Sugihara,† and Takehiko Nishio‡**

*Contribution from the Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338-8570, Japan, and Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan*

*Received June 1, 1998*

**Abstract:** Treatment of 1-chloro-2,2-bis(diethylamino)ethene (**1**) with elemental selenium in refluxing benzene gave 4,8-bis[bis(diethylamino)methylene]-1,2,3,5,6,7-hexaselenacyclooctane (**4**) in 60% yield. The structure of **4** was determined by X-ray diffraction analysis. Compound **4** behaves as 2,2-bis(diethylamino)-2-ethylium-1-diselenocarboxylate (**3**) toward a range of reagents. Thus, **4** reacted with MeI, dimethyl acetylenedicarboxylate, and elemental sulfur, under mild conditions, to give the carbenium iodide **5a**, the 1,3-diselenole **6a**, and the dithiocarboxylate **2**, respectively, in high yields, while the thermolysis in refluxing *o*-dichlorobenzene afforded the α-diselenoamide **7**. Evidence for the dissociation of **4** into **3** in solution is provided by IR, UV/vis, and $^1$H-, $^{13}$C-, and $^{77}$Se-NMR spectra.

2,2-Bis(dialkylamino)-2-ethylium-1-dithiocarboxylates are a structurally interesting, unique class of inner salts.[1,2] In recent several years, we have been investigating the synthesis, structure, and reactivities of 2,2-bis(diethylamino)-2-ethylium-1-dithiocarboxylate (**2**) and the related compounds.[3] Particularly, we have found that **2** is easily obtained in high yield by treatment of 1-chloro-2,2-bis(diethylamino)ethene (**1**)[4] with elemental sulfur in the presence of triethylamine at room temperature.[3a,b] We therefore thought that the reaction of **1** with elemental selenium would result in the formation of a new inner salt, 2,2-bis(diethylamino)-2-ethylium-1-diselenocarboxylate (**3**). Unexpectedly, however, the reaction gave the title compound, 4,8-bis[bis(diethylamino)methylene]-1,2,3,5,6,7-hexaselenacyclooctane (**4**), in good yield. We report the X-ray diffraction analysis of **4**, reactivities of **4** as the diselenocarboxylate **3** equivalent, and spectroscopic evidence for the formation of **3** in solution.



## Results and Discussion

**Synthesis.** Although the reaction of the enediamine **1** with sulfur took place smoothly to give **2** at room temperature in the presence of Et$_3$N, the reaction with gray metallic selenium did not proceed under the same conditions. However, the reaction took place in refluxing solvents such as benzene, toluene, and chlorobenzene. Thus, heating **1** with selenium in the presence of Et$_3$N in refluxing benzene for 5 h gave a 60% yield of a dark-red crystalline compound, mp 138.5−139.5 °C (dec.), that has an empirical formula of $(C_{10}H_{20}N_2Se_3)_n$. The structure of the compound could not be determined unequivocally by spectroscopies because of its highly complex but unique solution properties that will be discussed later. An X-ray single-crystal structure analysis revealed that the compound has the structure **4** ($n = 2$ in the empirical formula) which possesses a hitherto unknown hexaselenacyclooctane ring (Figure 1).[5] The compound adopts a typical crown-shaped conformation in the crystalline state. The C═C bond length (1.39 Å) of **4** is longer than those of the typical C═C bonds, and the torsion angle between the N−C−N and Se−C−Se planes is as large as 40.7°. These facts might suggest that the canonical structure **4′**

---

† Saitama University.

‡ University of Tsukuba.

(1) For a review, see: Nakayama, J. *Sulfur Lett.* **1993**, *15*, 239.

(2) (a) Winberg, H. E.; Coffman, D. D. *J. Am. Chem. Soc.* **1965**, *87*, 2776. (b) Clemens, D. H.; Bell, A. J.; O'Brien, J. L. *Tetrahedron Lett.* **1965**, 3257. (c) Schössler, W.; Regitz, M. *Chem. Ber.* **1974**, *107*, 1931. (d) Scheldrick, W. S.; Schönberg, A.; Singer, E.; Eckert, P. *Chem. Ber.* **1980**, *113*, 3605. (e) Krasuski, W.; Nikolaus, D.; Regitz, M. *Liebigs Ann. Chem.* **1982**, 1451. (f) Schönberg, A.; Singer, E.; Stephan, W. *Chem. Ber.* **1983**, *116*, 2068. (g) Schönberg, A.; Singer, E.; Stephan, W. *Chem. Ber.* **1984**, *117*, 3388.

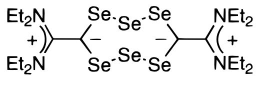
(3) (a) Nakayama, J.; Akiyama, I. *J. Chem. Soc., Chem. Commun.* **1992**, 1522. (b) Nagasawa, A.; Akiyama, I.; Mashima, S.; Nakayama, J. *Heteroat. Chem.* **1995**, *6*, 45. (c) Akimoto, K.; Nakayama, J. *Heteroat. Chem.* **1997**, *8*, 505. (d) Nakayama, J.; Otani, T.; Sugihara, Y.; Ishii, A. *Tetrahedron Lett.* **1997**, *38*, 5013. (e) Akimoto, K.; Masaki, K.; Nakayama, J. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 471. (f) Nakayama, J.; Otani, T.; Sugihara, Y.; Ishii, A. *Chem. Lett.* **1998**, 321.

(4) Delavarenne, S. Y.; Viehe, H. G. *Chem. Ber.* **1970**, *103*, 1209.

(5) For a review on eight-membered rings with four or more heteroatoms, see: Ollmann, R. R., Jr. In *Comprehensive Heterocyclic Chemistry* II; Newkome, G. R., Ed.; Pergamon: Oxford, U.K., 1996; Vol. 9, p 705.

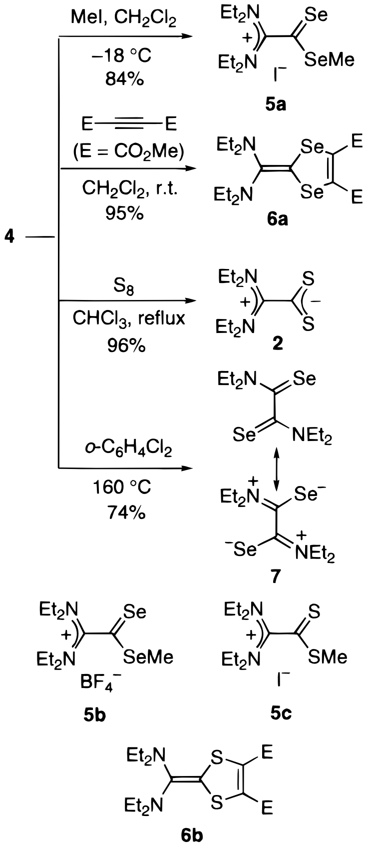
S0002-7863(98)01901-5 CCC: $15.00

contributes to the ground state of **4**.[6]

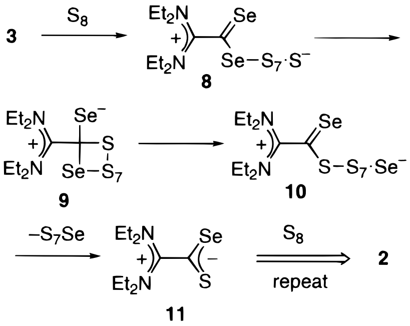


**4'**

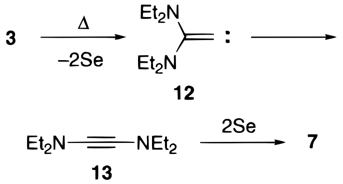
**Reactivities.** First of all, it is shown that **4** acts as 2,2-bis(diethylamino)-2-ethylium-1-diselenocarboxylate (**3**) on a range of reagents. Treatment of **4** with MeI at −18 °C resulted in a smooth reaction to give the carbenium iodide **5a** in 84% yield, revealing that **4** acted as **3** on MeI. The sulfur counterpart **2** is known to be methylated by MeI to give the carbenium iodide **5c** quantitatively.[3a,b] The iodide **5a** that possesses a diselenoic acid ester moiety[7] was obtained as beautiful dark-green needles which showed the longest $\lambda_{\max}$ at 575 nm ($\epsilon = 450$) in $CH_2Cl_2$. Treatment of **5a** with $AgBF_4$ afforded the tetrafluoroborate **5b** quantitatively. The reaction of **4** with dimethyl acetylenedicarboxylate (DMAD) proceeded at room temperature to give the 1,3-diselenole **6a** in 95% yield, which corresponds to the 1,3-dipolar cycloadduct of **3** with DMAD. The reaction provides a new 1,3-diselenole synthesis.[8] It is also known that **2** undergoes a 1,3-dipolar cycloaddition with DMAD to give the 1,3-dithiole **6b**.[3a,b]



When **4** was treated with sulfur in refluxing $CHCl_3$, a clean Se/S exchange reaction took place to give **2** in 96% yield. The reaction also proceeded at room temperature, though slowly. The nucleophilic attack of **3** on $S_8$ to give **8**, which is followed by ring opening and ring closure, would give rise to **10**. Elimination of $S_7Se$ from **10** would produce **11**, where one of the two selenium atoms of **3** was replaced by sulfur. The repetition of the same process will complete the exchange of one more selenium for sulfur.



Although **4** is rather thermally stable as is expected from the method of preparation, it decomposed to give the α-diselenoamide **7** in 74% yield, when heated at 160 °C in *o*-dichlorobenzene. The most probable mechanism for the formation of **7** would involve the elimination of two selenium atoms from **3** which gives the vinylidene carbene **12**. 1,2-Rearrangement of **12** to the ethyne **13**[9,10] and selenation of **13** by the selenium, so liberated, produce **7** as the final product. The preparation of **7** by selenation of **13** with elemental selenium was reported previously.[11] In the mass spectrum of **4** (EI, 20 and 70 eV), the only prominent peak appeared at *m/z* 168, which corresponds to the formula $[(Et_2N)_2C_2]$. The observation also supports the above mechanism.



**Spectroscopies.** The reactions described above are all indicative of the formation of the inner salt **3** from **4** in solution. Therefore, evidence for the existence of **3** should be searched in solutions. The IR spectra of **4** are given in Figure 2. In a $CH_2Cl_2$ solution, a new absorption, which was not observed in the solid state (KBr disk), appeared at 1545 $cm^{-1}$. It is known that compound **2** and the related inner salts show a strong absorption in a range of 1509−1610 $cm^{-1}$.[2e,3b] Such absorption is also observed with carbenium salts, **5a** (1563 $cm^{-1}$), **5b** (1582 $cm^{-1}$), and **5c** (1589 $cm^{-1}$).[3b] These facts suggest that **3** (or related species such as **14**), which are in equilibrium with **4**,

---

[6] The bond length between the carbenium and dithiocarboxylate (dithioester) carbons is 1.49 Å for **2**[3b] and 1.51 Å for **5c**.[3d] The torsion angle between the N−C−N and S−C−S planes is 82.0° for **2**[3b] and 72.6 ° for **5c**.[3d.]

[7] For the first successful synthesis of diselenoic acid esters, see: (a) Murai, T.; Mizutani, T.; Kanda, T.; Kato, S. *J. Am. Chem. Soc.* **1993**, *115*, 5823. (b) Murai, T.; Mizutani, T.; Kanda, T.; Kato, S. *Heteroat. Chem.* **1995**, *6*, 241. For a review, see: (c) Murai, T.; Kato, S. *Sulfur Rep.* **1998**, *20*, 397.

[8] For a recent review on 1,3-diselenoles, see: Becher, J.; Pedersen, C. Th.; Mørk, P. In *Comprehensive Heterocyclic Chemistry* II; Shinkai, I., Ed.; Pergamon: Oxford, U.K., 1996; Vol. 3, p 679.

[9] For reviews on 1,2-rearrangement of vinylidene carbenes, see: (a) Hartzler, H. D. In *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1974; Vol. 2, p 43. (b) Jones, W. M. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 2, p 95.

[10] The ethyne **13** is prepared by treatment of **1** with $Et_2NLi$.[4]

[11] (a) Nakayama, J.; Mizumura, A.; Akiyama, I.; Nishio, T.; Iida, I. *Chem. Lett.* **1994**, 77. See also (b) Borisenko, K. B.; Broschag, M.; Hargittai, I.; Klapötke, T. M.; Schröder, D.; Schultz, A.; Schwarz, H.; Tronieporth-Oetting, I. C.; White, P. S. *J. Chem. Soc., Dalton Trans.* **1994**, 2705. (c) Chesney, A.; Bryce, M. R.; Batsanov, A. S.; Howard, J. A. K. *J. Chem. Soc., Chem. Commun.* **1997**, 2293.

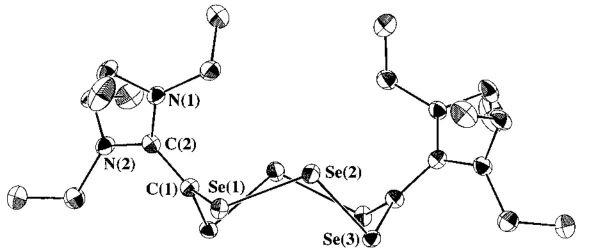


**Figure 1.** Molecular structure of **4** showing the labeling scheme at 50% probability ellipsoids. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Se(1)−Se(2), 2.370(1); Se(2)−Se(3), 2.343(1); Se(1)−C(1), 1.880(4); Se(3)−C(1), 1.901(4); C(1)−C(2), 1.389(6); C(2)−N(1), 1.371(5); C(2)−N(2), 1.372(5); Se(1)−Se(2)−Se(3), 107.0(1); Se(2)−Se(1)−C(1), 112.0(2); Se(2)−Se(3)−C(1), 101.6(2); Se(1)−C(1)−Se(3), 120.2(2); Se(1)−C(1)−C(2), 120.9(3); Se(3)−C(1)−C(2), 118.8(3); C(1)−C(2)−N(1), 122.3(4); C(1)−C(2)−N(2), 123.3(4); N(1)−C(2)−N(2), 114.3(4).

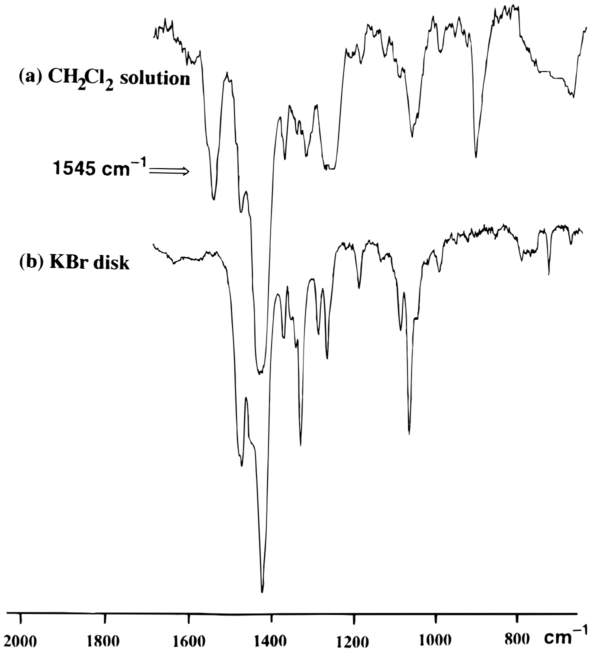
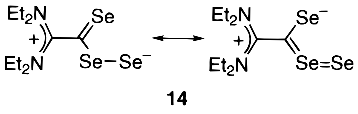


**Figure 2.** IR spectra of **4**: (a) $CH_2Cl_2$ solution; (b) KBr disk.

exists in $CH_2Cl_2$ solution.



**14**

Figure 3 shows the UV/vis spectra of **4** determined in a series of solvents of different polarity. In the nonpolar solvents, hexane and $CCl_4$, $\lambda_{max}$ at the longest wavelength appears at about 370 nm. In the more polar solvents, $CH_2Cl_2$ and $CHCl_3$, the absorption at 370 nm turns weak and a new strong $\lambda_{max}$ appears at about 440 nm instead. In the most polar solvent, dimethylformamide (DMF), a strong $\lambda_{max}$ is observed at 440 nm and the absorption is no longer seen at 370 nm. These bathochromic and hyperchromic shifts (the former reaches about 70 nm) cannot be explained in terms of simple solvent effect. The inner salt **2** shows the intense $\lambda_{max}$ at 368 nm ($\epsilon$ = 10 800).[3b] The corresponding absorption in the selenium counterpart **3** is expected to occur at a much longer wavelength. Incidentally, the bathochromic shift of 63 nm is observed on going from **5c** (333 nm; $\epsilon$ = 9270) to **5a** (396 nm; $\epsilon$ = 6600) for the comparison of the most intense $\lambda_{max}$. Therefore, it should be reasonable to assign the absorption at the 440 nm region to the ionized species **3** (or **14**) and the absorption at the 370 nm region to the hexaselenacyclooctane **4**. The assignment also agrees with the expectation that the formation of the ionized species is favored in polar solvents.

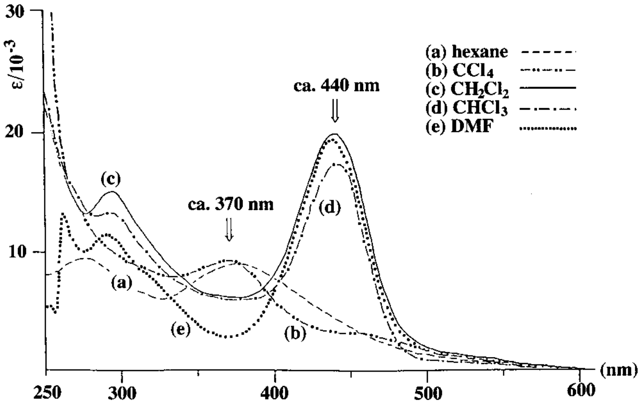


**Figure 3.** UV/vis spectra of **4** in various solvents: (a) hexane (—); (b) $CCl_4$ (−⋯−); (c) $CH_2Cl_2$ (--), (d) $CHCl_3$ (−•−); (e) DMF (⋯).

The $^1$H-NMR spectra of **4** do not show a simple $A_3X_2$ pattern, which is expected from the structural formula. The shape and chemical shift values of the ethyl signals much depend on solvent polarity and temperature. Thus, in $CD_2Cl_2$ at 25 °C, both the methyl and methylene signals consisted of two pairs of complex multiplets in nearly equal intensities (Figure 4). Homo-decoupling experiments confirmed that the methyl and methylene signals at the higher field constitutes a complementary pair. On lowering the temperature, the intensities of the higher field methyl and methylene signals increase with attenuation of the lower ones. At −16 °C the methyl and methylene pair at the lower field turns a typical $A_3X_2$ pattern, while at −98 °C all of the signals are broad. Comparison of the spectra in $CCl_4$, $C_6D_6$ (Figure 5), and $CD_2Cl_2$ (Figure 4) at 25 °C demonstrates how the shape and the chemical shift values of the ethyl signals are influenced by properties of the solvent. Particularly, a large higher field shift is seen in $C_6D_6$. In $CCl_4$, the intensity ratios of the higher and lower field signals of the methyl and methylene are about 10:1. Taking the results with UV/vis into consideration, the higher field signals in these $^1$H-NMR spectra might be ascribed to the hexaselenacyclooctane **4** and the lower field ones to the ionized species.

The number of the chemically nonequivalent carbons in structure **4** is only 4. However, the $^{13}$C-NMR spectrum showed at least 28 peaks in $CDCl_3$. Nearly 20 intense peaks, which originate from $CH_3$ and $CH_2$ of the ethyl groups, appeared in the ranges of $\delta$ 12−14 and 43−41, respectively. In addition, two weak peaks appeared at $\delta$ 75.5 and 85.8, six weak peaks at $\delta$ 163.8, 166.6, 169.5, 174.0, 174.1, and 178.1, and one weak peak at $\delta$ 234.6 (Figure 6). The thiocarbonyl carbon of **5c** appears at $\delta$ 215.3, and that of **2** moves to a lower field of $\delta$ 236.2. The selenocarbonyl carbon of **5a** appears at $\delta$ 213.7. Therefore, the last signal at $\delta$ 234.6 should be reasonably assigned to the selenocarbonyl carbon of the ionized species **3** (or **14**). Since the carbenium carbon atom of **2** occurs at $\delta$ 163.8, at least one of the six signals in the range of $\delta$ 164−178 should be ascribed to the carbenium carbon atom of **3** (**14**). The occurrence of a surprisingly great number of peaks in the $^{13}$C-NMR spectrum probably means that complex equilibrium exists in solution and that conformational change of some components, such as **4**, takes place.

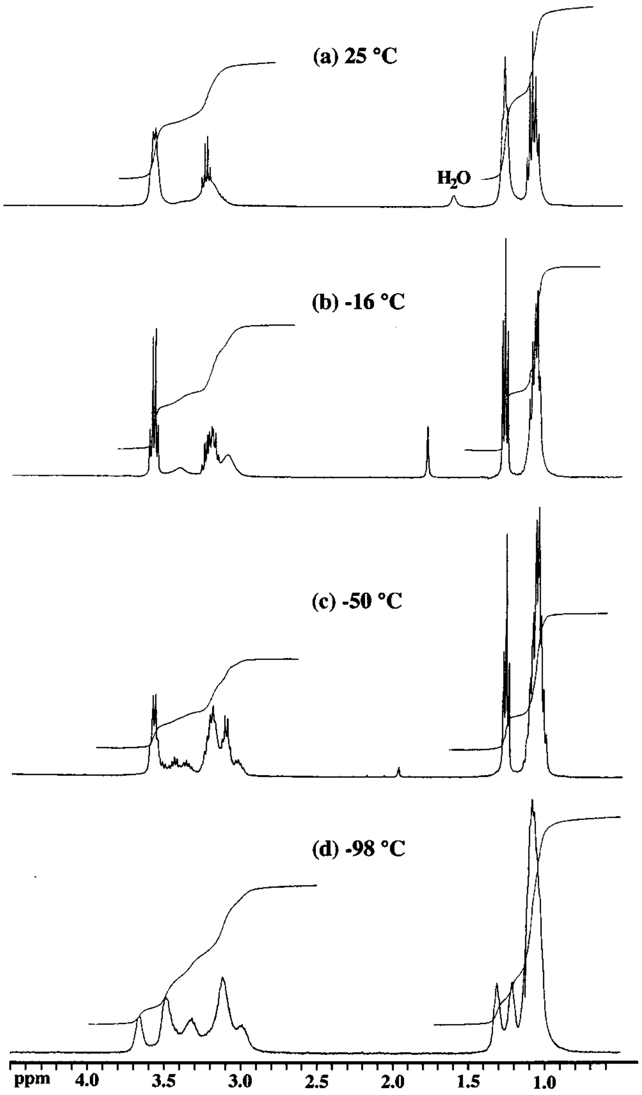


**Figure 4.** $^1$H-NMR spectra of **4** in $CD_2Cl_2$ at (a) +25, (b) −16, (c) −50, and (d) −98 °C.

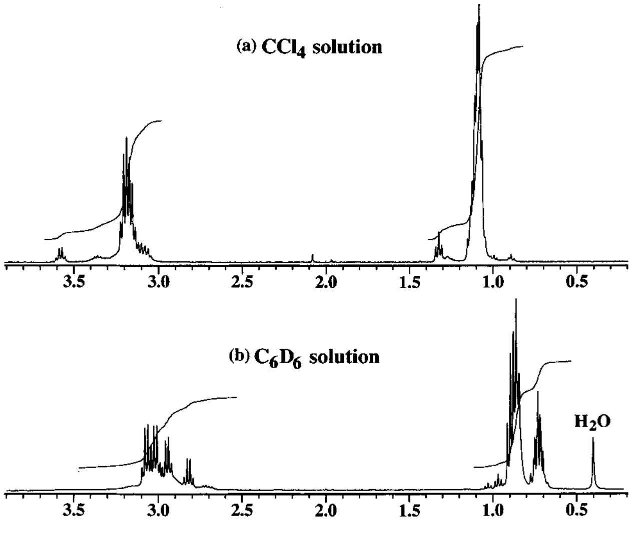


**Figure 5.** $^1$H-NMR spectrum of **4** at 25 °C in (a) $CCl_4$ and (b) $C_6D_6$.

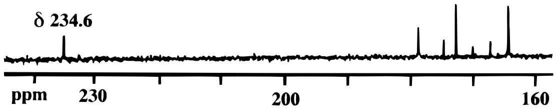


**Figure 6.** $^{13}$C NMR spectrum of **4** in $CDCl_3$ ($\delta$ 160−240 region).

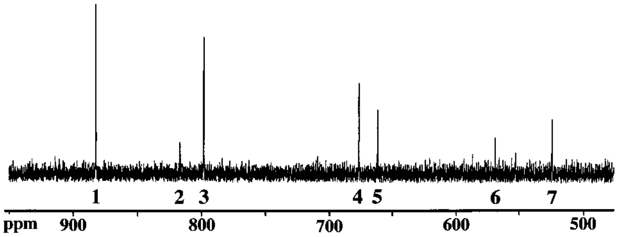
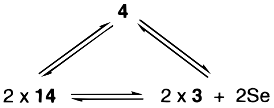


**Figure 7.** $^{77}$Se-NMR spectrum of **4** in $CDCl_3$ ($D_2SeO_3$ as the external standard).

Although the number of nonequivalent selenium atoms of **4** is only 2, the$^{77}$Se-NMR spectrum in $CD_2Cl_2$ gave seven peaks in the $\delta$ 500−900 region (Figure 7). The occurrence of the seven peaks is in harmony with the presence of the equilibrium shown as follows, though accidental agreement of the number of signals is not ruled out.



Finally it should be stressed that **4** is recovered quantitatively from its solution on the evaporation of the solvent.

In conclusion, the hexaselenacyclooctane **4** acts as the diselenocarboxylate **3** equivalent on a range of reagents, and the solution spectroscopies suggested that **4** dissociates into the ionized species containing **3** as the major component.

## Experimental Section

NMR ($^1$H, $^{13}$C, $^{77}$Se) spectra were recorded on a Bruker AM-400 or an ARX-400 spectrometer with tetramethylsilane ($\delta$ = 0.0, $^1$H NMR), $CDCl_3$ ($\delta$ = 77.0, $^{13}$C NMR), $CD_2Cl_2$ ($\delta$ = 53.8, $^{13}$C NMR) as internal standard and $D_2SeO_3$ ($\delta$ = 1282, $^{77}$Se NMR) as external standard. IR and UV/vis spectra were determined on a Hitachi 270-50 and a Shimadzu UV-160A spectrophotometer, respectively. Mass spectra (EI) were determined on a JEOL DX-303 spectrometer. Elemental analyses were performed by the Chemical Analysis Center of Saitama University. Merck 7734 Kiesel Gel (70−230 mesh ASTM) was used for silica gel column chromatography. Elemental selenium (Wako) was used as purchased. Melting points are uncorrected.

**4,8-Bis[bis(diethylamino)methylene]-1,2,3,5,6,7-hexaselenacyclooctane (4).** A mixture of **1** (3.26 g, 15.9 mmol), gray metallic selenium (5.04 g, 63.8 mmol), and $Et_3N$ (4.76 g, 47.1 mmol) in benzene (200 mL) was heated under reflux for 5 h under argon. The resulting precipitate of $Et_3N{\cdot}HCl$ was removed by filtration and the filtrate was evaporated under reduced pressure. The dark-red crystalline residue was triturated and washed with MeOH (100 mL) to give 3.84 g (60%) of practically pure **4**, mp 138.5−139.5 °C (dec.); crystallization of the above material (from $CH_2Cl_2$/MeOH, $CH_2Cl_2$/ether, $CCl_4$, etc.) did not raise the melting point. Anal. Calcd for $C_{20}H_{40}N_4Se_6$: C, 29.64; H, 4.98; N, 6.91. Found: C, 29.58; H, 4.86; N, 6.83.

**Bis(diethylamino)[methylseleno(selenocarbonyl)]carbenium Iodide (5a).** To a stirred solution of **4** (140 mg, 0.17 mmol) in $CH_2Cl_2$ (3 mL) was added a large excess of MeI (0.7 mL) at −18 °C under argon. The mixture was stirred for 20 min at −18 °C, and the resulting precipitate of selenium was removed by filtration. The filtrate was diluted with hexane and allowed to stand overnight in a refrigerator. The resulting dark-green needles were collected by filtration to give 136 mg (84%) of **5a**: mp 99.0−99.5 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.38 (t, $J$ = 7.2 Hz, 12H), 2.98 (s, 3H), 3.72 (m, 8H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 13.5 (q), 20.2 (q), 48.1 (t), 172.2 (s, $C^+$), 213.7 (s, C=S). IR (KBr, cm$^{-1}$): 1563, 1452, 1305, 916. UV/vis ($CH_2Cl_2$; $\lambda_{max}$, nm ($\epsilon$, $M^{-1}$ $cm^{-1}$)): 243 (20 300), 396 (6600), 575 (sh, 450). Anal. Calcd for $C_{11}H_{23}N_2ISe_2$: C, 28.22; H, 4.95; N, 5.98. Found: C, 28.32; H, 4.82; N, 5.96. Treatment of **5a** (100 mg, 0.21

mmol) with $AgBF_4$ (66 mg, 0.34 mmol) in $CH_2Cl_2$ gave the tetrafluoroborate salt **5b** (91 mg, 100%): mp 65−70 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.32 (t, $J$ = 7.1 Hz, 12H), 2.88 (s, 3H), 3.66 (m, 8H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 13.1 (q), 19.3 (q), 47.7 (t), 172.2 (s), 219.4 (s). Anal. Calcd for $C_{11}H_{23}N_2BF_4Se_2$: C, 30.87; H, 5.42; N, 6.54. Found: C, 30.99; H, 5.47; N, 6.78.

**2-Bis(diethylamino)methylene-4,5-bis(methoxycarbonyl)-1,3-diselenole (6a).** A mixture of **4** (280 mg, 0.35 mmol) and DMAD (108 mg, 0.76 mmol) in $CH_2Cl_2$ (5 mL) was stirred for 3 h at room temperature. The resulting precipitate of selenium was removed by filtration. The filtrate was evaporated under reduced pressure, and the crystalline residue was washed with a small amount of MeOH to give analytically pure **6a** (308 mg, 95%), dark-red plates: mp 54.5−56 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.02 (t, $J$ = 7.0 Hz, 12H), 2.86 (q, $J$ = 7.0 Hz, 8H), 3.78 (s, 6H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 14.3 (q), 44.4 (t), 52.8 (q), 87.7 (s), 134.3 (s), 143.4 (s), 163.2 (s). IR (KBr, $cm^{-1}$): 2964, 1731, 1701, 1562, 1270, 1242. MS: $m/z$ 470 ($M^+$). Anal. Calcd for $C_{16}H_{26}N_2O_4Se_2$: C, 41.04; H, 5.60; N, 5.98. Found: C. 41.08; H, 5.53; N, 5.95.

**2,2-Bis(diethylamino)-2-ethylium-1-dithiocarboxylate (2).** A mixture of **4** (85 mg, 0.1 mmol) and sulfur (27 mg, 0.1 mmol as $S_8$) in $CHCl_3$ (5 mL) was heated at reflux for 10 h under argon. The resulting precipitate of selenium was removed by filtration, and the filtrate was evaporated under reduced pressure. The crystalline residue was chromatographed on a column of silica gel. The column was eluted with hexane to give an excess of sulfur and then with $CH_2Cl_2$ to give 47 mg (96%) of **2**, mp 105−106 °C (lit.;[3a,b] mp 104.5−106.0 °C). Stirring a mixture of **4** (100 mg, 0.12 mmol) and sulfur (32 mg, 0.12 mmol) in chlorobenzene (5 mL) for 66 h at room temperature gave 51 mg (89%) of **2**.

**Tetraethylethanediselenoamide (7).** A solution of **4** (520 mg, 0.64 mmol) in *o*-dichlorobenzene (10 mL) was heated at 160 °C for 7 h under argon. The mixture was evaporated under reduced pressure. The residue was chromatographed on a column of silica gel. Elution with $CH_2Cl_2$ gave **7** (309 mg, 74%), mp 104−105 °C (lit.;[11a] mp 104.0−104.5 °C).

**X-ray Diffraction Analysis of 4.** Crystal data: $C_{20}H_{40}N_4Se_6$; $M_r$ = 810.33; orthorhombic; *Pcan*; $a$ = 13.075(1) Å, $b$ = 14.623(1) Å, $c$ = 15.383(1) Å, $V$ = 2891.2(3) Å$^3$, $Z$ = 4; D$x$ = 1.830 Mg m$^{-3}$; Mo K$\alpha$ radiation ($\lambda$ = 0.710 73 Å); $\mu$ = 74.052 mm$^{-1}$; $T$ = 153 K; crystal dimensions 0.42 × 0.35 × 0.35 mm. Data collection and cell refinement, Mac Science DIP3000 diffractometers, and data reduction, programs used to solve and refine the structure, and molecular graphics, CRYSTAN: 4473 measured reflections; 3321 independent reflections; $R$ = 0.034; $R_w$ = 0.039; $S$ = 2.377.

**Acknowledgment.** This work was supported by Grant-in-Aids (Nos. 10133206 and 09440213) for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan. We thank Dr. I. Iida of the University of Tsukuba for the assistance of the X-ray diffraction analysis of **4**.

**Supporting Information Available:** Figure showing ORTEP diagram of **4** and crystal data collection for **4** including tables of bond distances and angles, fractional atomic coordinates, and anisotropic thermal parameters (7 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA981901Z