

Selenium Coronands: Synthesis and Conformational Analysis¹

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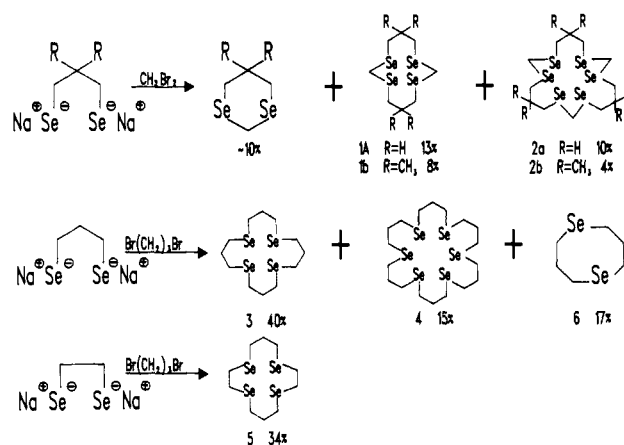
Abstract: The synthesis and characterization of the novel selenium coronands 1,3,7,9-tetraselenacyclododecane (**1a**), 1,3,7,9,13,15-hexaselenacyclooctadecane (**2a**), the corresponding *β*-gem-dimethyl derivatives **1b** and **2b**, 1,5,9,13-tetraselenacyclohexadecane (**3**), 1,5,9,13,17,21-hexaselenacyclotetracosane (**4**), and 1,4,8,11-tetraselenacyclotetradecane (**5**) are described. X-ray crystallographic analysis of **1a** reveals two distinct quadrangular conformations ([3333] and [66]) in both of which selenium atoms occupy alternate corner and side positions. **1a**: Se₄C₈H₁₆; fw = 428.05; space group P2₁/c; Z = 8; T = 200 K; a = 15.823 (2) Å; b = 5.534 (1) Å; c = 27.962 (5) Å; β = 92.26 (1)°; V = 2446.6 Å³; R_f = 0.027 for 2162 observed data. In contrast, DNMR studies in CFCl₃/CD₂Cl₂ (85:15) or CS₂/CD₂Cl₂ (85:15) show that the preferred conformation in solution of **1a** and its 5,5,11,11-tetramethyl analogue **1b** is a [3333] quadrangle with the selenium atoms occupying only side positions. Pseudorotational barriers of 6.0 and 7.6 kcal mol⁻¹ are calculated for **1a** and **1b**, respectively. Compound **2a** crystallizes in a unique irregular conformation dictated by gauche, gauche arrangements in the C-Se-C-Se-C fragments. Bond angle and torsion angle data, together with ²J_{Se-⁷⁷Se coupling constants in the solid-state CP-MAS ⁷⁷Se NMR spectrum, provide evidence for selenium anomeric (n_{Se}-σ*_{C-Se}) interactions. **2a**: Se₆C₁₂H₂₄; fw = 642.08; space group P2₁/c; Z = 4; T = 190 K; a = 20.154 (3) Å; b = 5.4292 (9) Å; c = 17.678 (3) Å; β = 110.66 (1)°; V = 1810.0 Å³; R_f = 0.024 for 2426 observed data. The best structural model for **3**, though not definitive, contains two ordered and one disordered molecule which are all [3535] quadrangles with selenium atoms in alternate corner and side positions on the long sides. **3**: Se₄C₁₂H₂₄; fw = 484.16; space group Cc; Z = 12; T = 160 K; a = 21.975 (5) Å; b = 18.073 (4) Å; c = 16.431 (7) Å; β = 132.16 (2)°; V = 4837.3 Å³; R_f = 0.070 for 2079 observed data. The structure of **4** contains a single conformer which, while not being quadrangular, can be visualized as arising from the compression of a [4848] quadrangle. **4**: Se₆C₁₈H₃₆; fw = 726.24; space group P1; Z = 1; T = 195 K; a = 5.279 (3) Å; b = 8.498 (3) Å; c = 14.224 (5) Å; α = 73.38 (3)°; β = 82.22 (4)°; γ = 88.85 (4)°; R_f = 0.041 for 1189 observed data. **5** crystallizes as a [3434] quadrangle with selenium atoms at the corners. **5**: Se₄C₁₀H₂₀; fw = 456.11; space group P2₁/c; Z = 2; T = 195 K; a = 5.4494 (6) Å; b = 15.875 (2) Å; c = 9.4666 (8) Å; β = 119.839 (8)°; V = 710.37 Å³; R_f = 0.023 for 1085 observed data. The solid-state CP-MAS ¹³C and ⁷⁷Se NMR spectra are in accord with the observed structures. The structural results show that there is a marked preference for gauche torsion angles about Se-C bonds as well as a further bias toward gauche torsion angles in the Se-C-Se-C fragments. The latter is evidence for a selenium anomeric effect.}

The study of synthetic ionophores such as crown ethers, coronands, cryptands, and podands is of current interest² from a structural viewpoint as well as a means of modeling the more complex natural host-guest complexes present in antibiotics and membrane transport systems. Macrocyclic polyoxa ethers (the crown ethers) have been extensively studied, and investigation of the corresponding polythia ethers is also well documented.³ For example, Rorabacher, Ochrymowycz, and co-workers⁴ pioneered work on the synthesis and investigation of the sulfur ligands and their copper complexes. More recently, Cooper and co-workers^{3,5} have made significant advances in the synthesis, conformational analysis, and coordination chemistry of macrocyclic polythia ethers. In particular, the relative stabilities of metal complexes have been linked to the degree of necessary conformational change from that of the uncomplexed ligands.³

Surprisingly, extension of this type of chemistry to the corresponding third-row analogues is virtually unknown. To the best of our knowledge, the only large-ring selenides reported to date are cyclic oligomers of selenoformaldehyde,⁶ diselenacyclophanes,⁷ macrocyclic diselena ethers,^{7b} and a selenium porphyrin derivative.⁸

Our interest in selenium coronands arose from the serendipitous finding that reaction of sodium propane-1,3-bis(selenolate) in liquid ammonia and THF with dibromomethane gave, in addition to 1,3-diselenane, significant amounts of macrocyclic polyselena ethers. This result, together with the findings of Cooper et al.⁹ that sulfur coronands possessed conformations that differed significantly from those of their oxygen counterparts and yielded metal complexes with unexpected electronic structures and redox properties, prompted us to investigate this route to selenium coronands in greater detail. We expected that the latter derivatives would preferentially bind softer metal ions.¹⁰

Scheme I



We report herein the synthesis and conformational analysis of the first examples of a novel class of selenium coronands, namely,

(1) Preliminary accounts of portions of this work have been published: Pinto, B. M.; Batchelor, R. J.; Johnston, B. D.; Einstein, F. W. B.; Gay, I. D. *J. Am. Chem. Soc.* **1988**, *110*, 2990. Pinto, B. M.; Johnston, B. D.; Batchelor, R. J.; Gu, J.-H. *J. Chem. Soc., Chem. Commun.* **1988**, 1087. Pinto, B. M.; Johnston, B. D.; Batchelor, R. J.; Einstein, F. W. B.; Gay, I. D. *Can. J. Chem.* **1988**, *66*, 2956.

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(3) For a recent review, see: Cooper, S. R. *Acc. Chem. Res.* **1988**, *21*, 141. See also: Schröder, M. *Pure Appl. Chem.* **1988**, *60*, 517.

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1,3,7,9-tetraselenacyclododecane (**1a**), 1,3,7,9,13,15-hexaselenacyclooctadecane (**2a**), the corresponding β -gem-dimethyl derivatives **1b** and **2b**, 1,5,9,13-tetraselenacyclohexadecane (**3**), 1,5,9,13,17,21-hexaselenacyclotetracosane (**4**), and 1,4,8,11-tetraselenacyclotetradecane **5** (Scheme 1).

Experimental Section

General Information. Melting points were determined on a Fisher-Johns melting-point apparatus and are uncorrected. ^1H NMR (400.13 MHz), ^{13}C NMR (100.6 MHz), and ^{77}Se NMR (76.3 MHz) spectra were recorded on a Bruker WM-400 NMR spectrometer. For the ^1H and ^{13}C NMR spectra, chemical shifts are given in ppm downfield from SiMe_4 . Chemical shifts and coupling constants were obtained from a first-order analysis of the spectra. For the ^{77}Se NMR spectra chemical shifts are given in ppm downfield from Me_2Se in CDCl_3 . The temperatures were measured in the following manner: Peak separations of the ^1H NMR signals from a standard methanol sample were converted into temperature values by using the quadratic equation of Van Geet,¹¹ scaled to 400 MHz,¹² and a calibration curve for the probe thermocouple was constructed. The temperatures were obtained from the above curve by extrapolation. Temperatures are believed to be accurate to ± 2 K.

Solid-state NMR spectra were recorded on an instrument (built in-house) operating at a field of 1.4 T. This produces resonance frequencies of 11.4 and 15.1 MHz for ^{77}Se and ^{13}C , respectively. Spectra were excited by using single-contact Hartmann-Hahn cross polarization. The matched radio frequency field strengths were 40 and 50 kHz for ^{77}Se and ^{13}C , respectively. The same field strength was used for proton decoupling during data acquisition. Samples were spun at the magic angle at frequencies of 2–3 kHz. The magic angle was correctly set within $\pm 0.1^\circ$ by optimizing the line width on well-crystallized samples of $(t\text{-Bu}_2\text{Sn})_2\text{Se}_2$ and $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. Chemical shifts were measured relative to long cylindrical samples of aqueous H_2SeO_3 and C_6H_6 . These were converted to shifts based on the standard Me_2Se and TMS scales by using literature data.

Chemical ionization mass spectra were measured on a Hewlett-Packard HP-5985 mass spectrometer with isobutane as the reacting gas.

Analytical TLC was performed on precoated aluminum plates with Merck silica gel 60F-254 as the absorbent. The developed plates were air dried, exposed to UV light and/or sprayed with 10% H_2SO_4 in ethanol, and heated to 100 $^\circ\text{C}$. Flash column chromatography was performed on Kieselgel 60 (230–400 mesh).¹³

Solvents were distilled before use and were dried, as necessary, by literature procedures. Reactions were performed under nitrogen by use

Table I. Physical Data for 1–6

compd	yield, %	mp or bp, $^\circ\text{C}$	formula	anal. calcd (found)	
				C	H
1a	10	136–137 (hexane)	$\text{C}_8\text{H}_{16}\text{Se}_4$	22.45 (22.53)	3.77 (3.80)
1b	8	174–176 (hexane)	$\text{C}_{12}\text{H}_{24}\text{Se}_4$	29.77 (29.64)	5.00 (5.01)
2a	5	57–58 (hexane)	$\text{C}_{12}\text{H}_{24}\text{Se}_6$	22.45 (22.51)	3.77 (3.61)
2b	4	107–108 (hexane)	$\text{C}_{18}\text{H}_{36}\text{Se}_6$	29.77 (29.81)	5.00 (5.10)
3	40	59–60 (hexane/EtOAc)	$\text{C}_{12}\text{H}_{24}\text{Se}_4$	29.77 (29.63)	5.00 (4.95)
4	15	39–40 (hexane/EtOAc)	$\text{C}_{18}\text{H}_{36}\text{Se}_6$	29.77 (29.63)	5.00 (4.97)
5	36	145–146 (EtOAc)	$\text{C}_{10}\text{H}_{20}\text{Se}_4$	26.13 (26.34)	4.38 (4.55)
6	17	100–110 (0.1 mmHg)	$\text{C}_6\text{H}_{12}\text{Se}_2$	29.77 (29.64)	5.00 (4.85)

of standard Schlenk tube techniques.

Microanalyses were performed by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

Synthesis. Typical Preparation. To propane-1,3-bis(selenocyanate) (2.53 g, 10.0 mmol) in liquid ammonia (100 mL) and dry THF (40 mL) was added Na metal in small pieces until a colorless homogeneous solution was obtained. A solution of 1,3-dibromopropane (1.1 mL, 11 mmol) in dry THF (60 mL) was added dropwise over 3.5 h. The ammonia was allowed to escape over 3 h, and the reaction mixture was diluted to 500 mL with water and extracted with methylene chloride (3×100 mL). The combined extracts were washed with water (100 mL), dried (MgSO_4), and concentrated in vacuo to yield a light orange oil which slowly partially crystallized. Purification by silica gel flash chromatography (hexane:ethyl acetate (20:1)) yielded 1,5-diselenacyclooctane (**6**) as a colorless oil (0.407 g, 17%), **3** as a colorless solid (0.963 g, 40%), and **4** as a colorless solid (0.351 g, 15%).

Details for the preparation of compounds **1a**, **1b**, **2a**, **2b**, and **5** are presented in the Results.

Spectroscopic Data. Mass Spectra. The isobutane chemical ionization mass spectra of 1–6 exhibited $M^+ + 1$ molecular ion isotopic clusters which correlated with the computer-simulated molecular ion patterns for the respective molecular formulas.

^1H NMR (400 MHz, CDCl_3). **1a**: δ 2.07 (4 H, 2 β - CH_2 's, pentet, $J = 7.1$ Hz, $^3J_{\text{H-Se}} = 7.0$ Hz), 2.86 (8 H, 4 α - CH_2 's, t, $J = 7.1$ Hz), 3.70 (4 H, 2-Se CH_2Se , s, $^2J_{\text{H-Se}} = 13.6$ Hz). **1b**: δ 1.11 (12 H, 4- CH_3 , s), 2.96 (8 H, 4 α - CH_2 's, s), 3.65 (4 H, 2-Se CH_2Se , s, $^2J_{\text{H-Se}} = 17.3$ Hz). **2a**: δ 2.11 (6 H, 3 β - CH_2 's, pentet, $J = 7.0$ Hz, $^3J_{\text{H-Se}} = 7.0$ Hz), 2.81 (12 H, 6 α - CH_2 's, t, $J = 7.0$ Hz), 3.69 (6 H, 3-Se CH_2Se , s, $^2J_{\text{H-Se}} = 13.7$ Hz). **2b**: δ 1.09 (18 H, 6 CH_3 , s), 2.81 (12 H, 6 α - CH_2 's, s), 3.68 (4 H, 3-Se CH_2Se , s, $^2J_{\text{H-Se}} = 14.5$ Hz). **3**: δ 2.06 (8 H, 4 β - CH_2 's, pentet, $J = 7.0$ Hz, $^3J_{\text{H-Se}} = 7.0$ Hz), 2.70 (16 H, 8 α - CH_2 's, t, $J = 7.0$ Hz, $^2J_{\text{H-Se}} = 11.0$ Hz). **4**: δ 2.03 (12 H, 6 β - CH_2 's, pentet, $J = 7.0$ Hz, $^3J_{\text{H-Se}} = 7.0$ Hz), 2.69 (24 H, 12 α - CH_2 's, t, $J = 7.0$ Hz, $^2J_{\text{H-Se}} = 11.0$ Hz). **5**: δ 2.10 (4 H, 2 β - CH_2 's, m), 2.68 (8 H, 4 α - CH_2 's, dd, $J = 15.7$ Hz), 2.91 (8 H, 4 α - CH_2 's, $J_{\text{H-Se}} = 9$ Hz). **6**: δ 2.24 (4 H, 2 β - CH_2 's, m), 2.88 (8 H, 4 α - CH_2 's, m).

^{13}C NMR (100 MHz, CDCl_3). **1a**: δ 13.0 (Se CH_2Se , t, $J_{\text{C-H}} = 154$ Hz, $^1J_{\text{C-Se}} = 87$ Hz), 25.5 (α - CH_2 's, t, $J_{\text{C-H}} = 140$ Hz, $^1J_{\text{C-Se}} = 63$ Hz), 29.3 (β - CH_2 's, t, $J_{\text{C-H}} = 129$ Hz). **1b**: δ 15.8 (Se CH_2Se , t, $J_{\text{C-H}} = 154$ Hz, $^1J_{\text{C-Se}} = 85$ Hz), 30.0 (CH_3 , q, $J_{\text{C-H}} = 123$ Hz), 35.4 (β -C's, s), 38.6 (α - CH_2 's, t, $J_{\text{C-H}} = 142$ Hz, $^1J_{\text{C-Se}} = 78$ Hz). **2a**: δ 14.0 (Se CH_2Se , t, $J_{\text{C-H}} = 154$ Hz, $^1J_{\text{C-Se}} = 83$ Hz), 26.1 (α - CH_2 's, t, $J_{\text{C-H}} = 142$ Hz, $^1J_{\text{C-Se}} = 63$ Hz), 30.7 (β - CH_2 's, t, $J_{\text{C-H}} = 129$ Hz). **2b**: δ 17.1 (Se CH_2Se , t, $J_{\text{C-H}} = 153$ Hz, $^1J_{\text{C-Se}} = 85$ Hz), 27.9 (CH_3 , q, $J_{\text{C-H}} = 123$ Hz), 36.2 (β -C's, s), 40.2 (α - CH_2 's, t, $J_{\text{C-H}} = 141$ Hz, $^1J_{\text{C-Se}} = 65$ Hz). **3**: δ 23.7 (α - CH_2 's, t, $J_{\text{C-H}} = 141$ Hz, $^1J_{\text{C-Se}} = 63$ Hz), 31.8 (β - CH_2 's, t, $J_{\text{C-H}} = 129$ Hz). **4**: δ 23.7 (α - CH_2 's, t, $J_{\text{C-H}} = 140$ Hz, $^1J_{\text{C-Se}} = 63$ Hz), 31.4 (β - CH_2 's, t, $J_{\text{C-H}} = 129$ Hz). **5**: δ 23.2 (α - CH_2 's, t, $J = 143$ Hz), 23.4 (α - CH_2 's, t, $J = 140$ Hz), 32.3 (β - CH_2 's, t, $J = 130$ Hz). **6**: δ 23.3 (α - CH_2 's, t, $J_{\text{C-H}} = 140$ Hz, $^1J_{\text{C-Se}} = 66$ Hz), 30.9 (β - CH_2 's, t, $J_{\text{C-H}} = 127$ Hz).

^{77}Se NMR (76 MHz, CDCl_3): **1a**, δ 192; **1b**, δ 145; **2a**, δ 203; **2b**, δ 154; **3**, δ 157; **4**, δ 153; **5**, δ 215; **6**, δ 137.

X-ray Crystallography. All crystals were mounted on Pyrex filaments by using epoxy resin. Measurements were made with an Enraf-Nonius CAD-4F diffractometer equipped with an extensively in-house-modified low-temperature attachment and using graphite-monochromatized radiation. Experimental details of the structure determinations of **1a**, **2a**, **4**, and **5** are summarized in Table II (**3** is discussed separately (see

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Table II. Experimental Details for the Structure Determinations of Selenium Coronands **1a**, **2a**, **4**, and **5**

	1a	2a	4	5
formula	Se ₄ C ₈ H ₁₆	Se ₆ C ₁₂ H ₂₄	Se ₆ C ₁₈ H ₃₆	Se ₄ C ₁₀ H ₂₀
cryst system	monoclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1̄	<i>P</i> 2 ₁ / <i>c</i>
temp, K	200	190	195	195
unit cell				
no. of rflctns/ θ range, deg	25/16.0–19.9	25/17.0–22.3	21/15.1–18.4	25/19.9–22.0
<i>a</i> , Å	15.823 (2)	20.154 (3)	5.279 (3)	5.4494 (6)
<i>b</i> , Å	5.534 (1)	5.4292 (9)	8.498 (3)	15.875 (2)
<i>c</i> , Å	27.962 (5)	17.678 (3)	14.224 (4)	9.4666 (8)
α , deg			73.38 (3)	
β , deg	92.26 (1)	110.66 (1)	82.22 (4)	119.839 (8)
γ , deg			88.85 (4)	
<i>V</i> , Å ³	2446.6	1810.0	605.7	710.37
<i>Z</i>	8	4	1	2
fw	428.05	642.08	726.24	456.11
ρ_e , g cm ⁻³	2.324	2.370	1.991	2.1324
μ (Mo K α), cm ⁻¹	118.3	120.0	89.74	101.96
cryst size, mm	0.11 × 0.21 × 0.48	0.10 × 0.21 × 0.55	0.015 × 0.23 × 0.35	0.10 × 0.15 × 0.40
λ , Å	0.71069	0.71069	0.71069	0.71069
transmission ^a	0.075–0.330	0.083–0.330	0.337–0.947	0.235–0.441
stds ^b no./rep time, h	2/1	2/1	2/1	2/1
scan mode	ω -2 θ	ω -2 θ	ω -2 θ	ω -2 θ
scan width, ^c deg	0.9 + 0.35 tan θ	0.9 + 0.35 tan θ	1.0 + 0.35 tan θ	0.98 + 0.35 tan θ
scan sp, ^d deg min ⁻¹	0.75–3.30	0.75–3.30	0.969–1.177	0.82–3.30
min–max 2 θ , deg	4–48	4–52	4–44	4–54
unique rflctns	3797	3539	1475	1528
obsd ^e rflctns	2162	2426	1189	1085
refined parameters	313	163	109	94
<i>R</i> ₁ ^f	0.027	0.024	0.041	0.023
<i>R</i> ₂ ^g	0.029 ^h	0.027 ^h	0.054 ⁱ	0.030 ^j
GOF ^k	1.03	1.00	1.44	0.99
diff max, e Å ⁻³	0.6 (2) ^l	0.7 (2) ^m	0.8 (2) ⁿ	0.4 (1) ^o
max, shift/error	0.08, ^p 0.22 ^q	0.01	0.01	0.01

^aAnalytical corrections for absorption applied to raw data after ref 14. ^bRep time is hours of acquisition time between repeat measurements of standards. In each case the standards showed no significant variations in intensity throughout data acquisition. ^cThe background intensities were estimated by extension of the predetermined scan angle by 25% on either side. ^dThe scan speed for each reflection was determined from the intensity of a preliminary scan. ^e $I \geq 2.5\sigma(I)$. ^f $R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|$; for observed data. ^g $R_2 = [\sum(w(|F_o| - |F_c|)^2) / \sum(wF_o^2)]^{1/2}$; for observed data. ^hUnit weights, $w = 1$. ⁱ $W = [\sigma^2(F) + 0.009F^2]^{-1}$. ^j $W = [\sigma^2(F) + 0.005F^2]^{-1}$. ^kGOF = $[\sum w(F_o - F_c)^2 / \text{degrees of freedom}]^{1/2}$. ^l1.12 Å from Se(303). ^m0.86 Å from Se(7). ⁿ0.99 Å from Se(9). ^o1.14 Å from Se(1). ^pNon-hydrogen variables. ^qHydrogen coordinates.

Table III. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å²) for the Se and C Atoms of **1a** at 200 K

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Se(101)	0.68391 (7)	0.72877 (24)	0.64785 (4)	3.33
Se(103)	0.62841 (6)	0.64491 (20)	0.75419 (4)	2.79
Se(107)	0.81499 (6)	1.26154 (21)	0.85184 (4)	2.92
Se(109)	0.92095 (6)	1.04717 (20)	0.76656 (3)	2.48
Se(201)	0.30648 (5)	-0.22172 (20)	0.53286 (3)	2.20
Se(203)	0.48195 (6)	-0.05581 (19)	0.58614 (3)	1.98
Se(301)	0.80846 (6)	0.72119 (21)	0.52825 (4)	2.44
Se(303)	0.97618 (6)	0.55654 (20)	0.58923 (4)	2.22
C(102)	0.6183 (7)	0.8582 (23)	0.6991 (4)	3.0
C(104)	0.5924 (7)	0.8684 (24)	0.8038 (4)	3.1
C(105)	0.6532 (6)	1.0722 (23)	0.8155 (4)	3.1
C(106)	0.7377 (7)	0.9908 (20)	0.8390 (4)	3.0
C(108)	0.8511 (6)	1.3133 (20)	0.7873 (4)	2.5
C(110)	0.9120 (7)	1.0940 (23)	0.6973 (4)	3.0
C(111)	0.8240 (7)	1.0486 (23)	0.6740 (4)	3.2
C(112)	0.7971 (6)	0.7916 (22)	0.6772 (4)	3.0
C(202)	0.3680 (6)	0.0425 (21)	0.5641 (4)	2.5
C(204)	0.5343 (6)	0.2676 (19)	0.5872 (4)	2.4
C(205)	0.5725 (6)	0.3309 (21)	0.5411 (4)	2.3
C(206)	0.6489 (6)	0.1748 (21)	0.5311 (3)	2.2
C(302)	0.8706 (8)	0.4534 (21)	0.5577 (5)	3.4
C(304)	1.0311 (7)	0.2367 (19)	0.5920 (4)	2.5
C(305)	1.0695 (6)	0.1696 (21)	0.5442 (4)	2.8
C(306)	1.1469 (6)	0.3120 (21)	0.5363 (4)	2.6

below)). After analytical corrections for absorption,¹⁴ data reduction was performed, including intensity scaling and Lorentz and polarization corrections. The positions of the Se atoms were determined by direct methods¹⁵ for **1a**, **2a**, and **5** while those of **4** were derived from a Pat-

Table IV. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å²) for the Se and C Atoms of **2a** at 190 K

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Se(1)	0.10307 (3)	0.54646 (11)	0.00060 (3)	1.59
Se(3)	0.14675 (3)	0.97138 (11)	0.14388 (3)	1.65
Se(7)	0.39884 (3)	1.34426 (13)	0.24866 (4)	2.15
Se(9)	0.49083 (3)	1.36661 (13)	0.12444 (4)	2.36
Se(13)	0.27804 (3)	0.79769 (11)	-0.03052 (4)	1.90
Se(15)	0.14624 (3)	1.11658 (11)	-0.15831 (4)	2.04
C(2)	0.0934 (3)	0.6727 (11)	0.0995 (3)	1.7
C(4)	0.2367 (3)	0.8055 (12)	0.2014 (4)	2.3
C(5)	0.2949 (3)	0.9877 (13)	0.2433 (4)	2.3
C(6)	0.3179 (3)	1.1405 (12)	0.1860 (4)	2.3
C(8)	0.4193 (3)	1.5085 (11)	0.1622 (3)	1.9
C(10)	0.4367 (3)	1.0976 (11)	0.0590 (4)	2.0
C(11)	0.3851 (3)	1.1732 (11)	-0.0245 (4)	2.0
C(12)	0.3440 (3)	0.9570 (13)	-0.0738 (4)	2.4
C(14)	0.2102 (3)	1.0669 (11)	-0.0478 (3)	1.9
C(16)	0.1001 (3)	0.7931 (12)	-0.1771 (3)	1.9
C(17)	0.0340 (3)	0.7683 (12)	-0.1566 (3)	1.9
C(18)	0.0433 (3)	0.8056 (11)	-0.0687 (3)	1.7

erson map. All carbon atoms were found from subsequent Fourier syntheses. All the hydrogen atoms for **1a** and **5** were located in difference maps, and for these structures final refinement included the coordinates of all atoms. For **2a** and **4**, most, but not all, of the hydrogen sites could be located in difference maps, and for these structures all the hydrogen atoms were placed in calculated positions and repositioned after further refinement of Se and C. In all four cases anisotropic temperature factors for Se and C were included in the final, full-matrix, least-squares re-

(15) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. MULTAN80, A System of Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data; Department of Physics, University of York, York, England, 1980.

Table V. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (\AA^2) for the Se and C Atoms of **4** at 195 K

atom	x	y	z	B_{eq}
Se(1)	0.73061 (21)	0.75039 (12)	0.01056 (7)	2.45
Se(5)	1.17706 (20)	0.87805 (12)	0.33714 (7)	2.40
Se(9)	0.32811 (20)	0.72617 (11)	0.66192 (7)	2.24
C(2)	0.7331 (18)	0.8726 (11)	0.1089 (7)	2.2
C(3)	0.9359 (19)	0.8291 (11)	0.1728 (7)	2.2
C(4)	0.9458 (20)	0.9439 (11)	0.2367 (7)	2.2
C(6)	0.9436 (20)	0.7197 (11)	0.4352 (7)	2.6
C(7)	0.7572 (19)	0.7890 (10)	0.5016 (6)	2.0
C(8)	0.5740 (20)	0.6559 (11)	0.5666 (7)	2.4
C(10)	0.5470 (20)	0.6936 (11)	0.7657 (7)	2.5
C(11)	0.5412 (18)	0.5163 (11)	0.8333 (7)	2.2
C(12)	0.2930 (18)	0.4719 (11)	0.9006 (7)	2.1

Table VI. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (\AA^2) for the Se and C Atoms of **5** at 195 K

atom	x	y	z	B_{eq}
Se(1)	-0.24069 (8)	0.53790 (3)	0.18222 (5)	2.09
Se(4)	0.46229 (9)	0.73933 (3)	0.48867 (5)	2.27
C(2)	0.0305 (9)	0.6110 (3)	0.3580 (5)	2.0
C(3)	0.2339 (9)	0.6567 (3)	0.3204 (5)	2.1
C(5)	0.6454 (9)	0.6649 (3)	0.6789 (5)	2.1
C(6)	0.8476 (9)	0.6024 (3)	0.6711 (4)	2.0
C(7)	0.9805 (9)	0.5462 (3)	0.8204 (5)	2.0

finements. For **5**, the reflection $-1, 0, 2$ suffered from extinction and was omitted from the refinement. Weighting schemes were chosen that leveled $(w(F_o - F_c)^2)$ as a function of both $(\sin \theta)/k$ and $|F_o|$. Positional and equivalent isotropic thermal parameters for the selenium and carbon atoms are given in Tables III–VI for **1a**, **2a**, **4**, and **5**, respectively. The coordinates and temperature factors for the hydrogen atoms as well as the anisotropic temperature factors for the non-hydrogen atoms and lists of observed and calculated structure factors for the four structures are deposited as supplementary material (see the paragraph at the end of the paper).

The solution and refinement of the structure of **3** were unsatisfactory.¹⁶ Data collected on two different crystals, one quadrant at 160 K and one hemisphere at room temperature, yielded similar results. Although the diffraction pattern could be indexed on an F -centered orthorhombic cell, the relative intensities of the data (corrected analytically¹⁴ for absorption) clearly indicated monoclinic symmetry. The structure was solved initially by direct methods¹⁵ in the space group $C2/c$. The best chemically reasonable model obtained in $C2/c$ yielded a residual of 11% but included considerable disorder. Extensive use of restraints were necessary to stabilize the refinement since interparameter correlation coefficients were high. This is, of course, consistent with the large number of parallel interatomic vectors resulting from the approximate higher symmetry of the structure.¹⁷ In addition to the uncertainty about the space group, the question of twinning was also carefully (but unsuccessfully) considered. Our most reasonable model ($R = 7.0\%$) is not twinned but has one of the three molecules in the asymmetric unit disordered in the space group Cc . There are restraints on all bond distances and angles, and the unreasonable behavior on their relaxation indicates clearly that this model is not a minimum for $\sum w\Delta^2$ (and implicitly " R "); one therefore cannot be confident that the result is definitive. We do not believe a better model (of comparable simplicity) can be obtained. Structural parameters for this model as well as observed and calculated structure factors are deposited as supplementary material.

The programs used for data reduction for all structures, and structure solution and refinement of **1a**, **2a**, **4**, and **5** were from the NRC VAX crystal structure system.¹⁸ The system CRYSTALS¹⁹ was used for the refinement of **3**. Complex scattering factors for neutral atoms²⁰ were used in the calculation of structure factors. Diagrams were generated

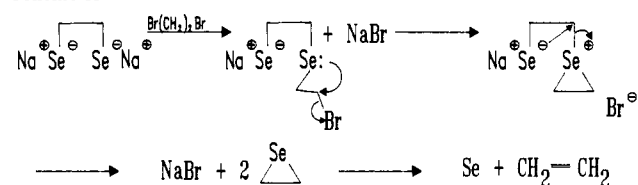
(16) $\text{Se}_4\text{C}_{12}\text{H}_{24}$; monoclinic; space group Cc , $T = 160$ K; $a = 21.975$ (5) \AA ; $b = 18.073$ (4) \AA ; $c = 16.431$ (7) \AA ; $\beta = 132.16$ (2) $^\circ$; $V = 4837.3$ \AA^3 ; $Z = 12$; $fw = 484.16$; $P_e = 1.994$ g cm^{-3} ; $\mu_{\text{MoK}\alpha} = 89.9$ cm^{-1} ; crystal size $0.25 \times 0.30 \times 0.45$ mm; transmission (Mo $K\alpha$) 0.090–0.142; 2079 observed data ($F \geq 5\sigma(F)$); 130 restraints; 232 refined parameters; $R_f = 0.067$.

(17) Geller, S. *Acta Crystallogr.* 1961, 14, 1026.

(18) Gabe, E. J.; Larson, A. C.; Lee, F. L.; LePage, Y. *NRC VAX Crystal Structure System*; Ottawa, Canada, National Research Council, 1984.

(19) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS*; Chemical Crystallography Laboratory; University of Oxford, 1985.

(20) International Tables for X-ray Crystallography; Kynoch Press: Birmingham, England, 1975; Vol. IV 99.

Scheme II

with the program SNOOPI.²¹ All computations were carried out on a MicroVax-II computer.

Results

Synthesis and Characterization. Reaction of sodium propane-1,3-bis(selenolate), derived from 1,3-propanebis(selenocyanate)^{22,23} by reduction with sodium in liquid ammonia, with dibromomethane in liquid ammonia and THF gave, in addition to 1,3-diselenane (10%), **1a** (10%) and **2a** (5%) as colorless solids (Scheme I). The rest of the reaction mixture appeared to consist of polymeric material. Similar treatment of 2,2-dimethylpropane-1,3-bis(selenolate), obtained by sodium reduction of 4,4-dimethyl-1,2-diselenolane^{23,24} in liquid ammonia, yielded crystalline **1b** and **2b**. The formation of the larger ring homologues of 1,3-diselenane in significant amounts was surprising, and we were stimulated to pursue this reaction type further. It is worth noting that even though the coronands are formed in low yield, they are nevertheless formed in a one-step reaction.

Extension of this approach to the preparation of coronands containing only three-carbon bridges proved to be more successful. Thus, treatment of sodium propane-1,3-bis(selenolate) with 1,3-dibromopropane afforded, in one step, **3** (40%), **4** (15%), and 1,5-diselenacyclooctane (**6**, 17%, Scheme I). The total yield of cyclic product (72%) is quite remarkable. The analogous reaction of sodium ethane-1,2-bis(selenolate)²⁵ with 1,3-dibromopropane afforded **5** in 36% yield. In the latter case, however, isolation proved to be difficult, significant decomposition occurring on the column during chromatography. We propose that **5** (and its higher homologues) decomposes to give ethylene and 1,2-diselenolane since an intense red color (characteristic of the latter species) was observed on the silica gel. The only other material isolated in low yield was 1,4-diselenacycloheptane.

Similar attempts to synthesize analogues with only two-carbon bridges, for example, the prototype coronand 18-crown-6, by reaction of sodium ethane-1,2-bis(selenolate)²⁵ with 1,2-dibromoethane were totally unsuccessful, with deposition of selenium and the extrusion of ethylene.²⁶ This likely arises because of the intermediate formation of the labile ethylene episelenide,²⁹ as shown in Scheme II (intermediacy of episelenonium ions has also been invoked in the nucleophilic substitution reactions of β -substituted selenides³⁰).

(21) Davies, E. K. SNOOPI Plot Program, Chemical Crystallography Laboratory, University of Oxford, Oxford, England, 1985.

(22) Clarebeau, M.; Cravador, A.; Dumont, W.; Hevesi, L.; Krief, A.; Lucchetti, J.; Van Ende, D. *Tetrahedron* 1985, 41, 4793.

(23) Pinto, B. M.; Johnston, B. D.; Nagelkerke, R. *Heterocycles* 1989, 28, 389.

(24) Backer, H. J.; Winter, H. J. *Recl. Trav. Chim. Pays-Bas* 1937, 91, 2703; Reich, H. J.; Hoeger, C. A.; Willis, W. W. Jr. *Tetrahedron* 1985, 41, 4771. Abel, E. A.; Mittel, P. K.; Orell, K. G.; Sik, V. *J. Chem. Soc., Dalton Trans.* 1985, 1569.

(25) Lakshminantham, M. V.; Cava, M. P. *J. Org. Chem.* 1980, 45, 2632.

(26) We are currently investigating alternate synthetic routes to selenium coronands involving stepwise syntheses. In addition, the optimization of yields of the reactions by studying the effects of high-dilution conditions²⁷ and the effects of cations such as cesium²⁸ are under way.

(27) For a review see: Rossa, L.; Vogtle, F. *Synthesis of Medio- and Macrocyclic Compounds by High Dilution Techniques*; *Top. Curr. Chem.* 1983, 113; Vogtle, F., Ed.; Springer-Verlag: New York.

(28) Dijkstra, G.; Kruizinga, W. H.; Kellogg, R. M. *J. Org. Chem.* 1987, 52, 4230; and references therein.

(29) Clive, D. L. J.; Denyer, C. V. *Chem. Commun.* 1973, 253. Chan, T. H.; Finkenbine, J. R. *Tetrahedron Lett.* 1974, 2091. Van Ende, D.; Krief, A. *Tetrahedron Lett.* 1975, 2709. Lakshminantham, M. V.; Cava, M. P. *J. Org. Chem.* 1976, 41, 879.

Table VII. Bond Distances and Angles and Torsion Angles for the Se and C atoms of **1a** at 200 K^a

Distances, Å			
Se(101)–C(102)	1.939 (11)	Se(101)C(112)	1.971 (10)
Se(103)–C(102)	1.942 (11)	Se(103)–C(104)	1.959 (12)
Se(107)–C(106)	1.958 (11)	Se(107)–C(108)	1.935 (10)
Se(109)–C(108)	1.943 (11)	Se(109)–C(110)	1.954 (12)
Se(201)–C(202)	1.945 (11)	Se(201)–C(206)'	1.965 (10)
Se(203)–C(202)	1.959 (10)	Se(203)–C(204)	1.972 (10)
Se(301)–C(302)	1.944 (12)	Se(301)–C(306)''	1.974 (11)
Se(303)–C(302)	1.943 (11)	Se(303)–C(304)	1.972 (10)
C(104)–C(105)	1.510 (17)	C(105)–C(106)	1.534 (15)
C(110)–C(111)	1.535 (15)	C(111)–C(112)	1.488 (17)
C(204)–C(205)	1.488 (15)	C(205)–C(206)	1.520 (14)
C(304)–C(305)	1.536 (15)	C(305)–C(306)	1.479 (15)
Angles, deg			
C(112)–Se(101)–C(102)	97.5 (5)	C(104)–Se(103)–C(102)	99.2 (5)
C(108)–Se(107)–C(106)	98.5 (5)	C(110)–Se(109)–C(108)	100.1 (5)
C(206)–Se(201)–C(202)	96.8 (5)	C(204)–Se(203)–C(202)	97.7 (5)
C(306)–Se(301)–C(302)	97.1 (6)	C(304)–Se(303)–C(302)	97.1 (5)
Se(103)–C(102)–Se(101)	109.4 (6)	C(105)–C(104)–Se(103)	115.1 (8)
C(106)–C(105)–C(104)	114.2 (10)	C(105)–C(106)–Se(107)	112.4 (8)
Se(109)–C(108)–Se(107)	111.0 (5)	C(111)–C(110)–Se(109)	115.3 (8)
C(112)–C(111)–C(110)	112.8 (10)	C(111)–C(112)–Se(101)	113.6 (8)
Se(203)–C(202)–Se(201)	111.8 (6)	C(205)–C(204)–Se(203)	112.7 (8)
C(206)–C(205)–C(204)	112.2 (9)	C(205)–C(206)–Se(201)'	114.2 (7)
Se(303)–C(302)–Se(301)	112.3 (6)	C(305)–C(304)–Se(303)	111.8 (8)
C(306)–C(305)–C(304)	111.0 (9)	C(305)–C(306)–Se(301)''	114.5 (8)
Torsion Angles, deg			
C(112)–Se(101)–C(102)–Se(103)	-70.6 (7)		
Se(101)–C(102)–Se(103)–C(104)	161.3 (7)		
C(102)–Se(103)–C(104)–C(105)	-69.1 (10)		
Se(103)–C(104)–C(105)–C(106)	-66.5 (12)		
C(104)–C(105)–C(106)–Se(107)	178.5 (12)		
C(105)–C(106)–Se(107)–C(108)	-76.4 (9)		
C(106)–Se(107)–C(108)–Se(109)	-69.1 (6)		
Se(107)–C(108)–Se(109)–C(110)	160.9 (7)		
C(108)–Se(109)–C(110)–C(111)	-67.4 (10)		
Se(109)–C(110)–C(111)–C(112)	-65.7 (12)		
C(110)–C(111)–C(112)–Se(101)	179.7 (15)		
C(111)–C(112)–Se(101)–C(102)	-77.4 (10)		
C(206)–Se(201)–C(202)–Se(203)	-85.0 (8)		
Se(201)–C(202)–Se(203)–C(204)	156.2 (6)		
C(202)–Se(203)–C(204)–C(205)	-90.7 (9)		
Se(203)–C(204)–C(205)–C(206)	-67.4 (10)		
C(204)–C(205)–C(206)–Se(201)'	172.8 (11)		
C(205)–C(206)–Se(201)–C(202)'	-94.7 (10)		
C(306)–Se(301)–C(302)–Se(303)	93.9 (8)		
Se(301)–C(302)–Se(303)–C(304)	-161.1 (7)		
C(302)–Se(303)–C(304)–C(305)	80.7 (9)		
Se(303)–C(304)–C(305)–C(306)	73.2 (10)		
C(304)–C(305)–C(306)–Se(301)''	-170.8 (12)		
C(305)–C(306)–Se(301)–C(302)''	90.6 (12)		

^aOne prime represents 1 - x, -y, 1 - z. Two primes represent 2 - x, 1 - y, 1 - z.

All compounds gave satisfactory combustion (C, H) microanalysis data. However, these data alone were not very informative owing to the oligomeric nature of the molecules. The actual structures were deduced by chemical ionization mass spectrometry. The isobutane chemical ionization mass spectra of **1–6** exhibited $M^+ + 1$ molecular ion isotopic clusters that correlated with the computer-simulated molecular ion patterns for the parent ions. The ¹H NMR and ¹³C NMR spectroscopic data are entirely in accord with the proposed structures. A noteworthy feature is the relatively low ¹³C chemical shift observed for the methylene carbon atoms flanked by two polarizable Se atoms in the Se–C–Se units²³ in **1a**, **2a**, and **2b**.

X-ray Crystallography. All bond distances found for **1a**, **2a**, **4**, and **5** are consistent with expected values for single covalent bonds. These are listed along with bond angles and torsion angles in Tables VII–X, respectively. Analogous parameters for **3** are deposited as supplementary material. Intermolecular distances are consistent with van der Waals interactions, except for Se contacts identified below for the individual structures. None of the structures display intramolecular contacts between atoms separated by more than three bonds that are less than the sum of the respective accepted van der Waals radii.

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Table VIII. Bond Distances and Angles and Torsion Angles for the Se and C Atoms of **2a** at 190 K

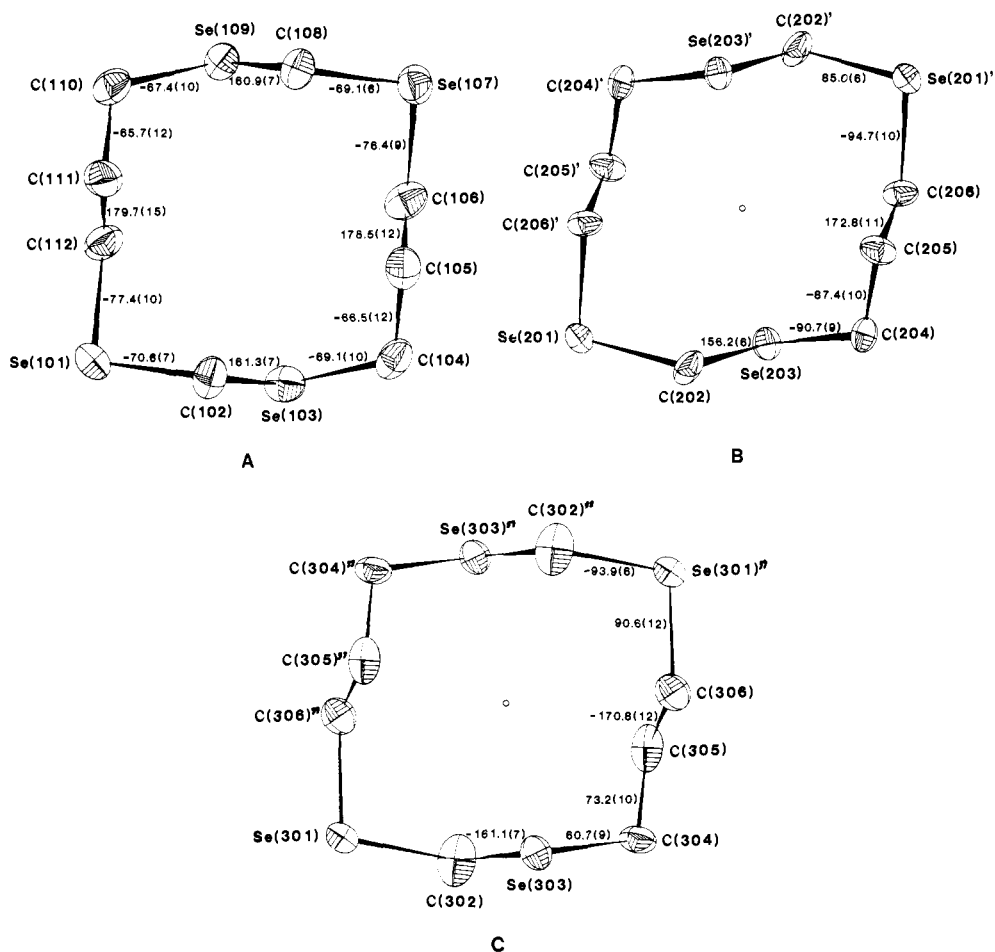
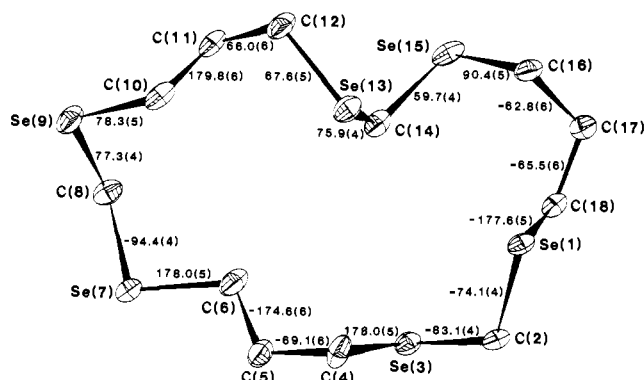
Distances, Å			
Se(1)–C(2)	1.947 (6)	Se(1)–C(18)	1.967 (6)
Se(3)–C(2)	1.946 (6)	Se(3)–C(4)	1.953 (6)
Se(7)–C(6)	1.955 (6)	Se(7)–C(8)	1.932 (6)
Se(9)–C(8)	1.944 (6)	Se(9)–C(10)	1.937 (6)
Se(13)–C(12)	1.951 (6)	Se(13)–C(14)	1.946 (6)
Se(15)–C(14)	1.939 (6)	Se(15)–C(16)	1.955 (7)
C(4)–C(5)	1.510 (9)	C(5)–C(6)	1.501 (9)
C(10)–C(11)	1.530 (9)	C(11)–C(12)	1.517 (9)
C(16)–C(17)	1.503 (9)	C(17)–C(18)	1.509 (8)
Angles, deg			
C(18)–Se(1)–C(2)	94.3 (3)	C(4)–Se(3)–C(2)	96.0 (3)
C(8)–Se(7)–C(6)	100.4 (3)	C(10)–Se(9)–C(8)	100.0 (3)
C(14)–Se(13)–C(12)	98.3 (3)	C(16)–Se(15)–C(14)	98.8 (3)
Se(3)–C(2)–Se(1)	116.0 (3)	C(5)–C(4)–Se(3)	111.8 (5)
C(6)–C(5)–C(4)	113.6 (6)	C(5)–C(6)–Se(7)	108.9 (4)
Se(9)–C(8)–Se(7)	118.6 (3)	C(11)–C(10)–Se(9)	114.9 (5)
C(12)–C(11)–C(10)	113.1 (6)	C(11)–C(12)–Se(13)	115.2 (4)
Se(15)–C(14)–Se(13)	116.2 (3)	C(17)–C(16)–Se(15)	116.6 (5)
C(18)–C(17)–C(16)	115.8 (5)	C(17)–C(18)–Se(1)	111.8 (4)
Torsion Angles, deg			
C(18)–Se(1)–C(2)–Se(3)	-74.1 (4)		
Se(1)–C(2)–Se(3)–C(4)	-83.1 (4)		
C(2)–Se(3)–C(4)–C(5)	178.0 (5)		
Se(3)–C(4)–C(5)–C(6)	-69.1 (6)		
C(4)–C(5)–C(6)–Se(7)	-174.8 (6)		
C(5)–C(6)–Se(7)–C(8)	178.0 (5)		
C(6)–Se(7)–C(8)–Se(9)	-94.4 (4)		
Se(7)–C(8)–Se(9)–C(10)	77.3 (4)		
C(8)–Se(9)–C(10)–C(11)	78.3 (5)		
Se(9)–C(10)–C(11)–C(12)	179.8 (8)		
C(10)–C(11)–C(12)–Se(13)	66.0 (6)		
C(11)–C(12)–Se(13)–C(14)	67.8 (5)		
C(12)–Se(13)–C(14)–Se(15)	75.9 (4)		
Se(13)–C(14)–Se(15)–C(16)	59.7 (4)		
C(14)–Se(15)–C(16)–C(17)	90.4 (5)		
Se(15)–C(16)–C(17)–C(18)	-62.8 (6)		
C(16)–C(17)–C(18)–Se(1)	-65.5 (6)		
C(17)–C(18)–Se(1)–C(2)	-177.6 (5)		

Table IX. Bond Distances and Angles and Torsion Angles for the Se and C Atoms of **4** at 195 K^a

Distances, Å			
Se(1)–C(2)	1.968 (10)	Se(1)–C(12)	1.944 (9)
Se(5)–C(4)	1.958 (11)	Se(5)–C(6)	1.950 (10)
Se(9)–C(8)	1.958 (10)	Se(9)–C(10)	1.951 (11)
C(2)–C(3)	1.471 (14)	C(3)–C(4)	1.517 (14)
C(6)–C(7)	1.500 (14)	C(7)–C(8)	1.508 (14)
C(10)–C(11)	1.536 (14)	C(11)–C(12)	1.500 (14)
Angles, deg			
C(12)–Se(1)–C(2)	99.1 (4)	C(6)–Se(5)–C(4)	96.6 (5)
C(10)–Se(9)–C(8)	96.8 (5)	C(3)–C(2)–Se(1)	115.6 (7)
C(4)–C(3)–C(2)	112.0 (8)	C(3)–C(4)–Se(5)	115.0 (7)
C(7)–C(6)–Se(5)	115.9 (7)	C(8)–C(7)–C(6)	110.0 (8)
C(7)–C(8)–Se(9)	114.7 (6)	C(11)–C(10)–Se(9)	113.6 (7)
C(12)–C(11)–C(10)	112.5 (8)	C(11)–C(12)–Se(1)	115.2 (7)
Torsion Angles, deg			
C(12)–Se(1)–C(2)–C(3)	56.4 (8)	Se(1)–C(2)–C(3)–C(4)	172.4 (10)
C(2)–C(3)–C(4)–Se(5)	171.9 (10)	C(3)–C(4)–Se(5)–C(6)	-81.8 (8)
C(4)–Se(5)–C(6)–C(7)	-84.6 (8)	Se(5)–C(6)–C(7)–C(8)	174.7 (10)
C(6)–C(7)–C(8)–Se(9)	177.3 (9)	C(7)–C(8)–Se(9)–C(10)	-85.6 (8)
C(8)–Se(9)–C(10)–C(11)	-84.7 (8)	Se(9)–C(10)–C(11)–C(12)	-71.4 (9)
C(10)–C(11)–C(12)–Se(1)	-179.7 (10)	C(11)–C(12)–Se(1)–C(2)'	-68.0 (8)

^aThe prime represents 1 - x, 1 - y, 1 - z.

The structure of **1a** contains three crystallographically independent molecules that exist in two distinct conformations. Ring A has no crystallographic symmetry but has an approximate 2-fold axis normal to the molecular plane, while rings B and C both lie on centers of inversion and have similar conformations (Figure 1). Ring A can be denoted as quadrangular [3333] in Dale's notation while rings B and C would be designated as "biangular" [66].³¹ That is, each of the four corners in ring A is formed by

Figure 1. Molecular structure of **1a**.Figure 2. Molecular structure of **2a**.

two gauche torsion angles of the same sign, whereas rings B and C have two such torsional sequences at opposite corners (with carbon as the pivotal atom) while the remaining corners (with selenium as the pivotal atom) are formed by consecutive gauche torsion angles of opposite sign. The former conformation was found for cyclododecane³² and 1,4,7,10-tetrathiacyclododecane,^{9,33} while the latter type occurs in 1,4,7,10-tetraoxacyclododecane.³⁴ The close Se...Se contacts are 3.691 (2) Å (Se(201)...Se(301)) and 3.695 (2) Å (Se(201)...Se(301)''), where the three primes represent $x, 1 + y, z$. The shortest nonbonded Se...C distance is 3.563 (10) Å (Se(301)...C(206)'').

The asymmetric unit of **2a** contains one molecule having a

Table X. Bond Distances and Angles and Torsion Angles for the Se and C Atoms of **5** at 195 K

Distances, Å			
Se(1)–C(2)	1.963 (5)	Se(1)–C(7)'	1.957 (5)
Se(4)–C(3)	1.958 (5)	Se(4)–C(5)	1.961 (5)
C(2)–C(3)	1.508 (6)	C(5)–C(6)	1.513 (6)
C(6)–C(7)	1.516 (6)		
Angles, deg			
C(2)–Se(1)–C(7)'	99.8 (2)	C(5)–Se(4)–C(3)	99.8 (2)
Se(1)–C(2)–C(3)	114.6 (3)	Se(4)–C(3)–C(2)	112.0 (3)
Se(4)–C(5)–C(6)	113.6 (3)	C(7)–C(6)–C(5)	111.2 (4)
Se(1)–C(7)–C(6)	113.7 (3)		
Torsion Angles, deg			
C(7)–Se(1)–C(2)–C(3)	65.8 (4)	Se(1)–C(2)–C(3)–Se(4)	172.3 (4)
C(2)–C(3)–Se(4)–C(5)	58.9 (4)	C(3)–Se(4)–C(5)–C(6)	66.2 (4)
Se(4)–C(5)–C(6)–C(7)	-179.5 (6)	C(5)–C(6)–C(7)–Se(1)'	179.0 (6)
C(6)–C(7)–Se(1)–C(2)'	-69.2 (4)		

^aThe prime represents $1 - x, 1 - y, 1 - z$.

unique irregular shape, in sharp contrast to the symmetrical quadrangular shapes normally exhibited by even-membered cycloalkane derivatives.³¹ The two long sides of the ring, shown in Figure 2, are distinctly different in character. The lower side of the ring, as shown, displays features typical of medium-sized macrocycles³¹ in that it is made up of approximately planar sequences, delineated by one or two anti torsion angles, which are connected by one or two bonds displaying gauche torsion angles. The upper side of the ring displays the unusual feature of an eight-atom helix, from C(10) to C(17), resulting from five consecutive gauche torsion angles of the same sign. The two sides are connected at the "corner" atom C(17) and by Se(9). Se(1), Se(3), and Se(15) can be described as endodentate, while Se(7), Se(9), and Se(15) are exodentate. The sequence of torsion angles about the ring, beginning at the Se(1)–C(2) bond, may be represented as G⁻G⁻AG⁻AAG⁻G⁺G⁺AG⁺G⁺G⁺G⁺G⁺G⁻G⁻A. An intermolecular Se...Se distance of 3.6228 (12) Å (Se(7)...Se(9)'),

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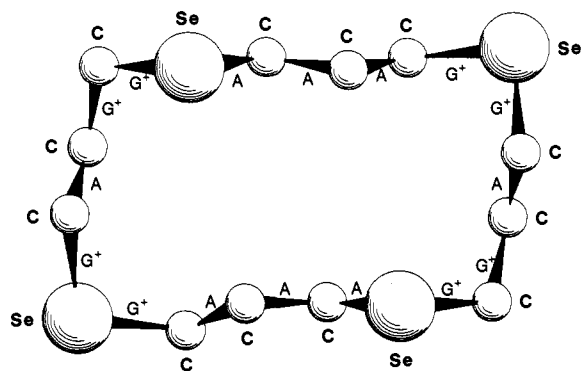


Figure 3. Molecular structure of 3.

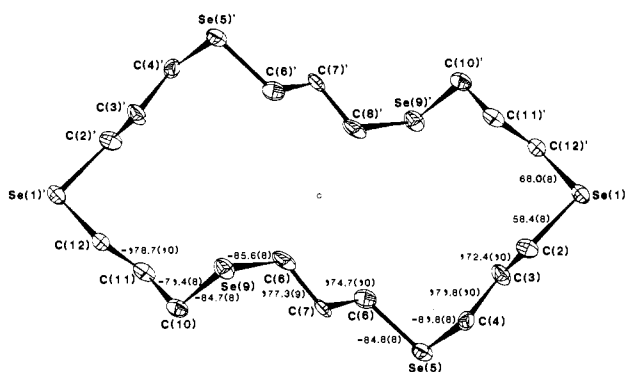


Figure 4. Molecular structure of 4.

$' = 1 - x, y - 1/2, 1/2 - z$ represents the only significant nonbonded contact.

The structural model for 3, while partially disordered and certainly suffering from a high degree of interparameter correlation, clearly reveals molecules of only one conformational type. In the space group *Cc* the asymmetric unit contains three molecules. The molecules are all [3535] quadrangles each having approximate 2-fold rotational symmetry about an axis perpendicular to the molecular plane. A representative example of the ring geometry is shown in Figure 3. The ranges of bond distances and of bond angles (restrained during structure refinement) are as follows: Se-C, 1.94–1.97 Å; C-C, 1.50–1.55 Å; C-Se-C, 97.4–99.8°; Se-C-C, 110.3–114.8°; C-C-C, 111.6–114.0°. The shortest Se...Se distance is an intermolecular contact of 3.45 (2) Å.

The structure of 4 contains a single conformer possessing crystallographic inversion symmetry. The sequence of torsion angles, beginning with the Se(1)–C(2) bond and progressing clockwise about the ring shown in Figure 4, can be described as G⁺AAG⁻G⁻AAG⁻G⁻AG⁻G⁻AAG⁺G⁺AAG⁺G⁺G⁺AG⁺. While not quadrangular in shape, this molecule can be visualized as deriving from a [4848] quadrangle with each long side buckled by replacing three anti torsion angles with three gauche torsion angles of the same sign. Thus, an asymmetric unit consisting of Se(9) through C(10)', proceeding clockwise in Figure 4, represents a "[443]" fragment, connected to its inversion related opposite by the bonds Se(9)–C(10) and Se(9)'–C(10)'. The connecting sequences of torsion angles from C(7) to C(12) (and C(7)' to C(12)') can be described as incipient helices. It is noteworthy that each selenium atom is situated between a pair of gauche torsion angles of the same sign. There are no significant nonbonded contacts.

The structure of 5 contains a single conformer lying on a crystallographic center of inversion (Figure 5). The molecule, which displays approximate 2/*m* point symmetry, is a [3434] quadrangle analogous to that in the α -form of its lighter congener, 1,4,8,11-tetrathiacyclotetradecane.³⁵ All four corner positions are occupied by selenium. The corner-to-corner packing of

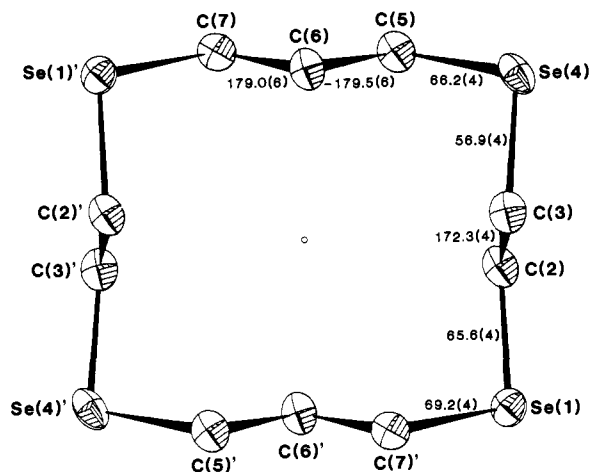


Figure 5. Molecular structure of 5.

Table XI. Solid-State CP-MAS ⁷⁷Se and ¹³C NMR Spectroscopic Data

compd	δ ⁷⁷ Se (rel int)	δ ¹³ C (rel int)
1a	130 (2), $W_{1/2} = 110$ Hz	11.2 (2)
	171 (1), $W_{1/2} = 20$ Hz, $J_{Se-Se} = 36$ Hz	17.6 (1)
	186 (2), $W_{1/2} = 35$ Hz	19.8 (1)
	196 (1)	25.2 (2)
	203 (1), $J_{Se-Se} = 31$ Hz	30.9
	209 (1), $J_{Se-Se} = 34$ Hz	32.1
		34.0
		35.3
		37.1
2a	136 (1), 188 (1), 206 (1), 216 (1)	16.0 (1)
	264 (1), $J_{Se-Se} = 128$ Hz	19.2 (1)
	327 (1), $J_{Se-Se} = 129$ Hz	20.2 (1)
		23.7 (1)
		25.7 (1)
		28.4 (2)
		29.7 (1)
3	115 (2), 118 (1), 157 (1), 165 (1), 177 (1)	20.2
		22.3
		24.7
		29.6
		30.1
		(1, br complex)
4	158 (1), 174 (1), 194 (1)	21.0 (2)
		26.2 (3)
		30.5 (1)
		34.3 (1)
		36.2 (2)
5	220 (1), 225 (1)	20.5 (1)
		21.8 (1)
		22.6 (2)
		22.6 (2)
		34.6 (1)

molecules in this structure results in a significant Se...Se contact (Se(1)...Se(1)') of 3.4111 (9) Å. Of the selenium coronand structures reported here, that of 5 displays the smallest estimated standard deviations (esd's). For this reason the anisotropic thermal motion was analyzed by using a rigid-body model for the molecule.³⁶ The weighted residual for observed and calculated U_{ij} was 10.8% and the root-mean-square discrepancy was 0.002 Å², which is comparable to the esd of an individual U_{ij} . Despite the good fit, the corrections to bond lengths, etc., are negligible compared to the errors, so they have not been listed.

Solid-State NMR Spectroscopy. The solid-state cross polarization-magic-angle spinning (CP-MAS) ⁷⁷Se and ¹³C NMR

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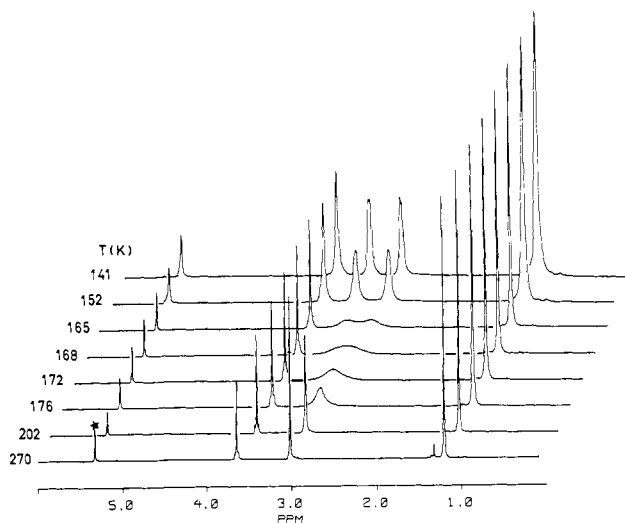


Figure 6. Variable-temperature ^1H NMR spectra of **1b** in $\text{CFCl}_3/\text{CD}_2\text{Cl}_2$ (85/15); the asterisk denotes the residual solvent peak.

spectra data for **1a**, **2a**, **3**, **4**, and **5** are listed in Table XI. The spectra are interpreted in light of the crystallographic information.

Dynamic NMR Studies. Of all the coronands examined, only **1a** and **1b** exhibited line-broadening effects due to chemical exchange in their NMR spectra in the accessible temperature range. Thus, the ^1H NMR spectrum of **1a** in $\text{CFCl}_3/\text{CD}_2\text{Cl}_2$ (85/15) exhibited the following behavior. Whereas the $\text{Se}-\text{CH}_2-\text{Se}$ (δ 3.56) and the $\text{C}-\text{CH}_2-\text{C}$ (δ 1.98) resonances remain unaffected as the temperature is lowered, the $\text{Se}-\text{CH}_2-\text{C}$ resonance (δ 2.82) broadens at about 165 K and reaches the coalescence point at 133 K, the practical low-temperature limit of our instrument. In contrast, the ^{77}Se and ^{13}C NMR spectra (down to 154 K) do not show any changes with temperature due to chemical exchange. The tetramethyl derivative **1b** behaves similarly to **1a**. However, in this case, the barriers to conformational interconversion are higher, and the ^1H NMR spectrum at the slow-exchange limit was obtained. The $\text{Se}-\text{CH}_2-\text{C}$ signal (δ 3.01) broadens at about 185 K and splits into two signals (δ 2.72, 3.10) below 165 K, whereas the $\text{Se}-\text{CH}_2-\text{Se}$ (δ 3.64) and methyl (δ 1.19) signals remain unchanged (Figure 6). The splitting of the $\text{Se}-\text{CH}_2-\text{C}$ signal to give an AB system ($^1J_{\text{AB}} = 9.5$ Hz, after resolution enhancement) at 141 K indicates that these geminal hydrogens are diastereotopic. As is the case with **1a**, the ^{77}Se and ^{13}C NMR spectra (down to 154 K) do not show any changes with temperature attributable to chemical exchange.

The free energy of activation for conformational interconversion in **1b** at the coalescence temperature, 167 K, was calculated by using the equation for a coalescing AB system, $\Delta G_c^\ddagger = 4.575 \cdot (10^{-3})T [9.972 + \log (T/(\delta\nu^2 + 6J_{\text{AB}}^2)^{1/2})]$ ³⁷ and was found to be ca. 7.6 kcal mol⁻¹. Similarly, ΔG_c^\ddagger in **1a** was estimated to be ca. 6.0 kcal mol⁻¹ ($T_c = 133$ K), assuming that $\Delta\nu$ and $^1J_{\text{AB}}$ for the exchanging protons are the same in **1a** and **1b**.

Discussion

The solid-state conformation of **1a** contrasts with the conformations of 1,4,7,10-tetrathiacyclododecane,^{9,33} in which S occupies exclusively the corner positions, and of 1,4,7,10-tetraoxacyclododecane,³⁴ in which O is found only in side positions. We note, however, the difference in connectivity between **1a** and the latter derivatives. The oxygen congener of **1a**, namely, 1,3,7,9-tetraoxacyclododecane, has been reported to exist in solution in a preferred conformation with the oxygen atoms occupying only side positions.³⁸

The asymmetric unit of **1a** is composed of 8 Se and 16 C atoms. The solid-state CP-MAS ^{77}Se NMR spectrum consists of six resolved resonances (δ 209–130) of relative intensity 1:1:1:2:1:2,

some of which exhibit Se–Se coupling (Table XI). The line width of the peak at highest field is such that the individual unresolved resonances must be of considerably larger line width than the others. We note that Se(101) and Se(107) show the largest thermal motion and assign the highest field peak to these atoms.³⁹ The solid-state CP-MAS ^{13}C NMR spectrum of **1a** is also consistent with the proposed structure. The resonances at δ 19.8, 17.6, and 11.2, of intensities 1:1:2, are assigned to the carbons of the four independent $\text{Se}-\text{CH}_2-\text{Se}$ units. The high-field shifts appear to be characteristic of this structural unit.²³ Structurally, each of these four atoms has one gauche and one anti $\text{Se}-\text{C}^*-\text{Se}-\text{C}$ arrangement, the atoms being distinguished by differences in the torsion angles. The angles for $\text{C}^*(102)$ and $\text{C}^*(108)$ are not significantly different, suggesting the assignment of the peak at δ 11.2 to these atoms. We note also that in the latter case, the gauche torsion angles are larger than in the other two $\text{Se}-\text{CH}_2-\text{Se}$ units and suggest that the shielding of these carbon atoms is linked to the greater $n_{\text{Se}}-\sigma^*_{\text{C}-\text{Se}}$ anomeric interactions²³ (see below).

The ^1H NMR spectrum of **1b** at 141 K (Figure 6) is consistent only with a preferred conformation displaying 2-fold rotational symmetry axes that bisect the $\text{CH}_2-\text{CMe}_2-\text{CH}_2$ and $\text{Se}-\text{CH}_2-\text{Se}$ groups. The assignment presumes that the $\text{Se}-\text{CH}_2-\text{Se}$ and Me_2 signals do not split because the groups are stereochemically equivalent and not because the signals are accidentally isochronous. In support of this contention, we have observed similar dynamic behavior in another solvent, $\text{CS}_2/\text{CD}_2\text{Cl}_2$ (85/15). **1a** shows analogous dynamic behavior although the barrier to pseudorotation is lower. We propose that **1a** and **1b** undergo site exchange as shown in Figure 7.^{31b} Similar conformational behavior has been observed³⁸ for the oxygen congener, 1,3,7,9-tetraoxacyclododecane, and its 2,2,8,8-tetramethyl derivative.

While the placement of heteroatoms (X) across corners can be rationalized^{40–42} in terms of minimization of 1,4 $\text{CH}\cdots\text{CH}$ contacts, and maximization of 1,4 $\text{CH}\cdots\text{X}$ attractive interactions,⁴³ we note also that such placement is consistent with expectations based on the anomeric effect^{44,45} (see below). Molecular mechanics (MacroModel⁴⁶) calculations of analogous conformations for oxygen and sulfur species corresponding to **1a** show that the solution conformation is lower in energy than those in the solid [$\Delta H(\text{O analogue}) > \Delta H(\text{S analogue})$]. We expect the corresponding difference between conformations in the selenium analogue **1a** to be even less.

The conformational barriers for **1a** and **1b** (6.0 and 7.6 kcal mol⁻¹, respectively) are of comparable magnitude to those in cyclododecane (7.3 kcal mol⁻¹)⁴⁸ and cyclodecanone (7.3 kcal mol⁻¹)⁴⁹ and those for the two processes in 1,4,7,10-tetraoxacy-

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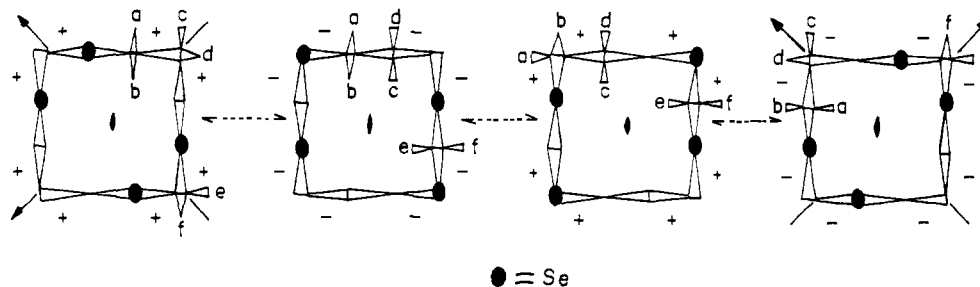


Figure 7. Conformational interconversion pathway for **1a** and **1b**; **1a**, $a = b = c = d = e = f = \text{H}$; **1b**, $a = b = e = f = \text{H}$, $c = d = \text{Me}$.

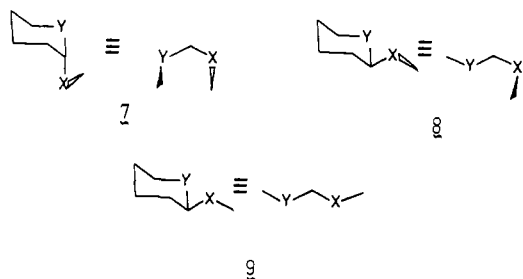


Figure 8. Conformations of $\text{RX-CH}_2\text{-YR}'$ molecules and their relationships to the conformations of 2-substituted heterocyclohexanes.

clododecane ($5.5, 6.8 \text{ kcal mol}^{-1}$)⁵⁰ but are much lower than that in the oxygen congener (11 kcal mol^{-1}).³⁸ The latter difference is attributable to the relative ground-state stabilization of the oxygen compound, although some contribution from the alleviation of syn-eclipsing interactions in the transition state for pseudorotation in **1a** and **1b**, because of the longer C-Se bonds, cannot be ruled out.

The conformation of **2a** is best analyzed in terms of the preferred torsion angles for the different four-atom sequences, Se-C-C-C, C-Se-C-C, and Se-C-Se-C. It has been suggested,⁹ on the basis of a consideration of 1,4 interactions, that gauche preferences about C-X bonds should decrease in the order $\text{C-S} \gg \text{C-C} > \text{C-O}$. Similarly, we find that the gauche torsion angles of **2a** are found preferentially about C-Se bonds. More importantly, however, gauche torsion angles are displayed by 6 out of 6 Se-C-Se-C sequences but only by 3 out of 6 C-Se-C-C sequences. We take the marked preference by the former as evidence for the existence of a selenium anomeric effect, which thus appears to be the dominating influence on the overall molecular conformation.⁵¹ The unimposed intermolecular Se...Se contact might contribute to stabilizing the molecular conformation of **2a**.

In its generalized form, the anomeric effect refers to the torsional preferences about the C-X and C-Y bonds in $\text{RX-CH}_2\text{-YR}'$ molecules. The conformations increase in energy in the sequence gauche, gauche **7** < anti, gauche **8** < anti, anti **9** (Figure 8). The behavior has been rationalized by a perturbational molecular orbital (PMO) treatment that focuses on the stabilizing orbital interactions between the p-type nonbonding orbitals on X and Y, n_X and n_Y , with the acceptor orbitals, $\sigma^*_{\text{C-Y}}$ and $\sigma^*_{\text{C-X}}$, respectively.^{52,53} Whereas both these interactions may be expressed in **7**, symmetry considerations dictate that only the $n_X\text{-}\sigma^*_{\text{C-Y}}$ interaction is possible in **8** and neither interaction is possible in **9**. These hyperconjugative interactions account for the existence of the endo and exo anomeric effect^{54,55} when the

$\text{RX-CH}_2\text{-YR}'$ moiety is incorporated into a heterocyclohexane (Figure 8).

We interpret the preference for gauche, gauche arrangements in the C-Se-C-Se-C units of **2a** as a manifestation of a selenium anomeric effect, despite questions recently raised as to the existence of significant anomeric interactions involving second and lower row elements.^{56,57} A strong analogous preference for gauche, gauche arrangements in C-O-C-O-C fragments has been noted in oxygen coronands containing 1,3-dioxa groupings.⁴²

The solid-state CP-MAS ⁷⁷Se NMR spectrum of **2a** displays six peaks of equal area (Table XI). The two resonances at lowest field have been assigned to Se(7) (326.5 ppm) and Se(9) (264.3) on the basis of (1) the broader line width of the resonance at 264 ppm which we associate with more rapid relaxation due to the greater average thermal motion of Se(9)³⁹ and (2) their relatively large mutual spin-spin coupling constant, $^2J_{\text{Se-Se}} = 128 \text{ Hz}$. These atoms display the largest C-Se-C and Se-C-Se bond angles in the molecule, implying maximal s-orbital character in the connecting bonds. The latter point is of significance since expression of the anomeric effect is predicted to open up the X-C-Y bond angle.^{58,59} Apparently, the Se-C-Se anomeric effect is maximized in the Se(7)-C(8)-Se(9) fragment relative to the other two similar units. It is interesting to note that the largest gauche torsion angle ($94.4 (4)^\circ$) is found in the former unit. This result, together with the corresponding result for **1a**, suggests that the optimum geometry required for expression of $n_{\text{Se}}\text{-}\sigma^*_{\text{C-Se}}$ anomeric interactions is one involving "gauche" torsion angles that are near 90° .⁵³

The solid-state CP-MAS ¹³C NMR spectrum of **2a** displays nine resolved peaks of relative areas 1:3:1:2:1:1:1:1:1 (Table XI) and is consistent with the presence of 12 unique carbon sites in the asymmetric unit. As in the case of **1a**, we suggest the assignment of the three highest field peaks to the three methylene carbon atoms of the Se-C-Se units.²³

Attempts to confirm the molecular conformation of **2a** in solution by ⁷⁷Se and ¹H NMR spectroscopy at 145 K were unsuccessful because of rapid site exchange. Similar experiments with the β -gem-dimethyl derivative **2b**, in which the barriers to pseudorotation were expected to be higher, were unfortunately frustrated by problems of solubility.

The molecules of **3**, have a [3535] rather than the [4444] "ideally unstrained" conformation in which all Se atoms could occupy corners, that is, all C-Se-C-C sequences would have gauche torsion angles. The tendency for large cycloalkane rings to favor slightly strained, compact quadrangular conformations over the more open, unstrained ones has been noted by Dale.³¹

The CP-MAS ⁷⁷Se NMR spectrum of **3** shows five resolved resonances whose relative intensities are 2:1:1:1:1. The spectrum is consistent with the presence of three molecules in the asymmetric unit, each having approximate 2-fold rotational symmetry. Unfortunately, the CP-MAS ¹³C NMR spectrum shows two broad complex envelopes with only some clearly resolved resonances

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(Table XI), making it difficult to comment further.

The conformation of **4** contrasts with that of **3** as well as the hydrocarbon analogue, cyclotetrasiloxane, which adopts a compact [3939] quadrangular conformation.^{60,61} This difference may be attributable to the preference for gauche torsion angles about Se-C bonds. It is thus noteworthy that every Se-C bond has a gauche C-Se-C-C torsion angle.

The CP-MAS ⁷⁷Se NMR spectrum of **4** shows only three resonances of equal intensity, consistent with the presence of a single conformer having crystallographic inversion symmetry. Also consistent is the CP-MAS ¹³C NMR spectrum, which shows five resolved resonances in a ratio of 2:3:1:1:2, accounting for the nine unique carbon sites in the asymmetric unit.

The placement of the selenium atoms in corner positions of **5** confirms the preference for the gauche torsion angles to occur about Se-C bonds. Of the structures reported here this is the only one to conform to the "diamond lattice" formalism.

The CP-MAS ⁷⁷Se NMR spectrum of **5** shows two peaks, as expected because of the crystallographic center of inversion. The CP-MAS ¹³C NMR spectrum shows four resolved resonances in the ratio of 1:1:2:1, consistent with the presence of five unique carbon sites in the molecule.

The potential ability of coronands **3**, **4**, and **5** to serve as complexing agents for soft metal ions is currently under investigation, compounds **1a**, **1b**, **2a**, and **2b** being considered as less likely candidates owing to restrictions imposed by the connectivities in the latter derivatives. In this regard, several complexes of **3** and

4 with Cu(I), Cu(II), Ag(I), and Pd(II) ions have been prepared.⁶²

Conclusions

All the structures display a preference for gauche torsion angles about the Se-C bonds. The crystal structure of **2a** as well as the solution conformation of **1a** and **1b** show, in addition, a bias toward gauche torsion angles about the bonds to the "anomeric" carbon atoms. The crystal structures of **1a** and **3** show that these preferences can be overridden by other effects such as crystal packing and the tendency of the larger rings to adopt compact conformations (rather than more open, ideally unstrained conformations). The largest rings **2a** and **4** display compact conformations that feature sequences of gauche torsion angles of the same sign, in contrast to the large, even-membered cycloalkanes, which feature two long parallel sides composed of sequences of anti torsion angles.

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Supplementary Material Available: Table of experimental details for the X-ray structural analysis of **3**, table of atomic coordinates and isotropic or equivalent isotropic thermal parameters for **3**, tables of hydrogen atom coordinates and isotropic thermal parameters for **1a**, **2a**, **4**, and **5**, tables of anisotropic thermal parameters for Se and C atoms of **1a**, **2a**, **4**, and **5**, table of anisotropic thermal parameters for Se atoms of **3**, tables of bond distances, bond angles, and torsion angles for **3** (22 pages); tables of observed and calculated structure factors for **1a**, **2a**, **3**, **4**, and **5** (67 pages). Ordering information is given on any current masthead page.

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Properties and Reactivity of Metallocarboxylates. Characterization of Aquobis(ethylenediamine)(hydroxycarbonyl)cobalt(III) [(H₂O)(en)₂Co(C(O)OH)]²⁺ and Its Ethyl Ester, *trans*-[Co(en)₂(CF₃CO₂)(C(O)OC₂H₅)]PF₆

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Abstract: The title metallocarboxylate, first described by Vaudo et al. (*J. Am. Chem. Soc.* 1972, *94*, 6655) has been further investigated, and its ethyl ester, prepared. Crystals of the ester (ethoxycarbonyl) [Co(NH₂CH₂CH₂NH₂)₂(O₂CCF₃)(C(O)OC₂H₅)]PF₆ are monoclinic: space group *P*2₁/*c* with *a* = 9.077 (1) Å, *b* = 16.375 (2) Å, *c* = 12.919 (2) Å, β = 92.15 (1)°, *V* = 1918.9 (7) Å³, *Z* = 4, and refined to a final *R* value of 0.079. The ethylenediamine ligands are trans to one another (Co-N ave, 1.944 (13) Å) with axial ligands CF₃CO₂⁻ (Co-O, 2.046 (7) Å) and -C(O)OC₂H₅⁻ (Co-C, 1.922 (9) Å; C=O 1.196 (9) Å, ν_{C=O} 1645 cm⁻¹). The aquo hydroxycarbonyl complex (UV-vis: λ_{max}, nm [ε, M⁻¹ cm⁻¹] 410 [125], 314 sh [580], 262 [5200]) is a dibasic acid with p*K*₁ = 2.5 ± 0.5 and p*K*₂ = 3.7 ± 0.5 at 15 °C and 0.5 M ionic strength and, at pH > 5, is present as the neutral hydroxy-oxycarbonyl complex Co(en)₂(OH)(CO₂) (UV-vis: 450 [100], 357 [245], 318 [280], 266 [9000]). The aquo ethoxycarbonyl complex (UV-vis: 424 [113], 320 sh [210], 264 [5100]) is a monobasic acid with p*K*_a = 8.7 ± 0.2 at 25 °C and 0.5 M ionic strength and, at high pH, is converted to Co(en)₂(OH)(CO₂Et)⁺ (UV-vis: 430 [159], 329 sh [260]). The ethoxy function is hydrolyzed very slowly in the latter complexes (pH, *k*_{obsd}: 1, 2.5 × 10⁻⁶ s⁻¹; 7, <2 × 10⁻⁷ s⁻¹; 13, 3 × 10⁻⁶ s⁻¹) to yield ethanol and the hydroxy- or oxycarbonyl, depending upon the pH. At pH > 0 the oxy- or hydroxycarbonyl complex undergoes decomposition through the singly protonated Co(en)₂(H₂O)(CO₂)⁺, exhibiting a rate maximum (*k*_{obsd} ≈ 3 × 10⁻³ s⁻¹, 25 °C) at ca. pH 3.2.

Metallocarboxylate (oxycarbonyl) complexes play an important role in diverse reactions of catalytic importance.³ Under water-gas

shift conditions,⁴ they may be formed by nucleophilic attack of hydroxide ion on a metal carbonyl. In this context, the rate and