ligand, observed on addition of the two alkali-metal ions.

Formation constants of PhDTA complexes of these alkali-metal ions are again smaller than those of the other amino polycarboxylate ligands.[6,22] Since the change in entropy is not so different among the complexes of these ligands, endothermicity is evidently responsible for the reduced reactivity of PhDTA.[8]

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Registry No. PhDTA, 40774-59-2; Na, 7440-23-5; Li, 7439-93-2.

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A New Type of Macrocycle Incorporating *closo*- and *nido*-Carborane Cages: Molecular Structures of 1,2-(1,10-Dithia-4,7-dioxadecane-1,10-diyl)-1,2-dicarba-*closo*-dodecaborane and Sodium 7,8-(1,13-Dithia-4,7,10-trioxatridecane-1,13-diyl)-7,8-dicarba-*nido*-undecaborate(12)

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One of the most differentiating characteristics of macrocycles is the existence of a cavity, which causes most of their peculiar properties. The combination of this cavity with other chemical subunits such as chelating moieties or other groups to form bi- or polycycles should form molecular species with specific features. Eventually these species could mimic not only the active site of an enzyme but also its function.

Recently, Lehn and co-workers have indicated the importance of lateral macrobicyclic cryptands as coreceptor molecules[1] based on the combination of two binding subunits, one that is chelating and the other macrocyclic, stressing the interest in having a soft, redox-active site combined with a hard Lewis acid center to activate a substrate and consequently form a cascade complex. Dinuclear macrocyclic and macropolycyclic ligands have been actively studied in recent years.[2,3]

Some of us reported earlier the synthesis and in one case the crystal structure of other macrocycles containing two 7,8-dicarba-nido-undecaborate(12) subunits, which present an anti disposition.[4] We describe here the synthesis of a new type of macrocycle that combines a "soft" 7,8-dicarba-*nido*-undecaborate(12) unit with the hard thioxa macrocycles [12]-O_2S_2 and [15]-O_3S_2. Nondegraded species and the crystal structures of sodium 7,8-(1,13-dithia-4,7,10-trioxatridecane-1,13-diyl)-7,8-dicarba-*nido*-undecaborate(12) and 1,2-(1,10-dithia-4,7-dioxadecane-1,10-diyl)-1,2-dicarba-*closo*-dodecaborane are also described.[5]

Experimental Section

Before use, *o*-carborane (I) (Dexsil Chemical Corp.) was sublimed; *o*-carborane-1,2-dithiol (II) was prepared from *o*-carborane according to the literature.[6] A 1.7 M solution of *n*-butyllithium in hexane (Fluka or Aldrich) and 1,2-bis(2-chloroethoxy)ethane (Aldrich) were used as given. 1,11-Dichloro-3,6,9-trioxoundecane was synthesized from the appropriate alcohol (tetraethylene glycol)[7] and RhCl $(PPh_3)_3$ was synthesized according to the literature.[8]

Elemental analyses were performed in our analytical laboratory by using a Perkin-Elmer 240-B microanalyzer. The ^1H NMR spectra were obtained by using a Bruker AM 400 WB instrument. IR spectra were obtained with KBr pellets on a Perkin-Elmer 240FT spectrophotometer.

Synthesis of 1,2-(1,10-Dithia-4,7-dioxadecane-1,10-diyl)-1,2-dicarba-*closo*-dodecaborane (III) and Trimethylammonium 7,8-(1,10-Dithia-4,7-dioxadecane-1,10-diyl)-7,8-dicarbaundecaborate(12) (IV). Under a dinitrogen atmosphere, the dichloride 1,2-bis(2-chloroethoxy)ethane (1.346 g, 7.2 mmol) was dissolved in degassed absolute ethanol (52 mL). Sodium hydroxide (0.578 g, 14.4 mmol) and *o*-carborane-1,2-dithiol (1.5 g, 7.2 mmol) were dissolved in 52 mL of the same solvent. By means of a syringe pump, the dichloride and the *o*-carborane-1,2-dithiolate solutions were then added simultaneously from syringes, at a rate of 4 mL h^{-1} onto refluxing degassed absolute ethanol (250 mL), contained in a round-bottom flask equipped with three condensers. To avoid the fast contact of the two reacting solutions, the syringe tubes were discharged into the lateral condensers.

After the addition, the mixture was kept stirring and refluxing for an additional 3 h period. Once the mixture was cooled to room temperature, a white solid (NaCl) was separated by filtration. The bulk of the solvent was then evaporated, and water and ethyl ether were added. The water layer was washed with more ether and kept to isolate IV and V.

Separation of 1,2-(1,10-Dithia-4,7-dioxadecane-1,10-diyl)-1,2-dicarba-*closo*-dodecaborane (III). The combined ether fractions were washed with a water/NaOH solution, discarding the aqueous phase. The ether solution was dried (anhydrous Na_2SO_4, 24 h), and evaporated to yield a yellowish oil. This was chromatographed on alumina by using ethyl ether as eluent. The solution was evaporated, and again, the oily product chromatographed as before. After partial evaporation of the solvent and on standing, white crystals of III appeared. IR (KBr): ν(C–H), 2932, 2861 cm^{-1}; ν(C–O–C), 1125 cm^{-1}; ν(B–H), 2571 cm^{-1}. MS at *m/z* (relative intensity): M, molecular peak centered at 323 (4,2%); 279 (7,9%), M – CH_2CH_2O; 234 (41,1%), M – $CH_2CH_2OCH_2CH_2O$; 207 (23,8%), M – $CH_2CH_2OCH_2CH_2OCH_2CH_2$. ^1H NMR (ppm, acetone-d_6) 3.76 (m, 2, O–CH_2), 3.60 (m, 2, O–CH_2), 2.93 (m, 2, S–CH_2). ^{13}C NMR (ppm, acetone-d_6, BB decoupled): 71.64 (s, O–CH_2), 70.1 (s, O–CH_2), 37.45 (s, S–CH_2). Anal. Calcd: C, 29.81; H, 6.83. Found: C, 30.0; H, 6.9.

Separation of Trimethylammonium 7,8-(1,10-Dithia-4,7-dioxadecane-1,10-diyl)-7,8-dicarbaundecaborate(12) (IV) and V. The water layer was treated with excess trimethylammonium chloride to precipitate an off-white solid (IV), which was filtered, washed with water and ether, and vacuum-dried. Yield: 1.12 g (41.6%). IR (KBr): ν(C–H) and ν-(N^+–H), 3024–2865 cm^{-1}; ν(B–H), 2520 cm^{-1}; ν(C–O–C), 1117 cm^{-1}. ^1H NMR (ppm, acetone-d_6): 3.77 (m, 2, O–CH_2), 3.61 (m, 2, O–CH_2), 3.43 (s, 12, $N(CH_3)_4$), 2.95 (m, 2, S–CH_2). ^{13}C NMR (ppm, acetone-d_6, BB decoupled): 71.79 (s, O–CH_2), 69.95 (s, O–CH_2), 55.77 (t, N-$(CH_3)_4$), 37.01 (s, S–CH_2). Anal. Calcd: C, 35.56; N, 3.77; H, 8.62. Found: C, 35.2; N, 3.8; H, 8.6.

If tetramethylammonium chloride is used instead of the trimethylammonium salt, tetramethylammonium 7,8-(1,10-dithia-4,7-dioxadecane-1,10-diyl)-7,8-dicarbaundecaborate(12) is obtained (V).

Synthesis of Sodium 7,8-(1,13-Dithia-4,7,10-trioxatridecane-1,13-diyl)-7,8-dicarba-*nido*-undecaborate(12) (VI). The starting procedure

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(5) For these macrocycles we have adopted the following convention: The macrocycle is closed via the carborane's two carbons, so these two are included in the counting scheme; e.g., C–S–$(CH_2–CH_2–O)_2$–CH_2–C-H_2–S–C has 12 links and is indicated as [12]-O_2S_2. For the nomenclature of the macrocycles, these have been considered as derivatives of the carborane using the current convention.

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Table I. Crystal Data and Details of Intensity Collection

	III	VI
space group	$P2_1$	$Pnma$
a, Å	9.681 (9)	15.615 (2)
b, Å	22.424 (7)	13.851 (3)
c, Å	7.983 (5)	9.076 (1)
β, deg	96.18 (8)	
V, Å^3	1722.9	1963.0
d(calcd), g cm^{-3}	1.24	1.50
Z	4	4
cryst dimens, mm	0.25 × 0.32 × 0.27	0.18 × 0.17 × 0.22
radiation	Mo Kα	Mo Kα
abs coeff (μ), cm^{-1}	2.895	4.955
scan speed, deg/min	2.5	2.5
max 2θ, deg	47	50
total no. of reflcns	5216	3708
no. of unique data, $I > 2.5\sigma(I)$	2145	1413
R, %	4.2	6.3
R_w, %	4.6	6.9
residual $\Delta\rho$, Å^{-3}	0.5, −0.4	0.55, −0.57

is as indicated for the synthesis of III–V, with 1,11-dichloro-3,6,9-trioxoundecane (1.548 g, 7.2 mmol) used as the dichloride compound. *o*-Carborane-1,2-dithiol (1.5 g, 7.2 mmol) and NaOH (578 mg, 14.4 mmol) were dissolved in 37 mL of degassed absolute ethanol (rate 3 mL h^{-1}). After the elimination of the NaCl, the bulk of the solvent was then evaporated and water and ethyl ether were added. Usually, an emulsion was formed, which slowly yielded a white solid (VI). This was filtered, washed with ethyl ether, and vacuum-dried. Yield: 0.99 g (36.4%). IR (KBr): ν(C–H), 2879 cm^{-1}; ν(C–O–C), 1099 cm^{-1}; ν(B–H), 2593 cm^{-1}. ^{1}H NMR (ppm, acetone-d_6): 8.0 (s, 1, +H), 3.67 (m, 12, O–CH_2), 2.99 (m, 4, S–CH_2). ^{13}C NMR (ppm, acetone-d_6, BB decoupled): 69.9 (s, O–CH$_2$), 69.4 (s, O–CH$_2$), 69.1 (s, O–CH$_2$), 37.8 (s, S–CH$_2$). Anal. Calcd: C, 31.73; H, 6.87. Found: C, 31.8; H, 6.9.

A portion of the crude product was dissolved in hot ethanol, which after a week yielded white, good quality crystals appropriate for X-ray diffraction analysis. Both the aqueous and ethereal layers were studied, but only unreacted materials were found.

Synthesis of $(PPh_3)_2RhH[7,8\text{-}SCB_9H_9CSCH_2(CH_2OCH_2)_3CH_2]$ (VII). To a round-bottom three-necked flask equipped with a condenser and containing 20 mL of degassed absolute ethanol were added sodium 7,8-(1,13-dithia-4,7,10-trioxatridecane-1,13-diyl)-7,8-dicarba-*nido*-undecaborate(12) (82 mg, 0.216 mmol) and RhCl(PPh$_3$)$_3$ (0.2 g, 0.216 mmol). The mixture was kept at reflux for 0.5 h, yielding an orange-yellow solid that was filtered by Schlenk techniques. The air-stable compound was recrystallized by using an acetone/toluene mixture; however, the crystals rapidly lost solvent molecules, which made it difficult to work with them. Yield: 137 mg (64.5%). IR (KBr): ν(aromatic C–H), 3053 cm^{-1}; ν(C–H), 2863–2947 cm^{-1}; ν(B–H), 2550 cm^{-1}; ν(C–O–C), 1094 cm^{-1}. ^{1}H NMR (ppm): 7.2 (30, aromatic H), 3.65 (12, OCH_2), 2.67 (4, SCH_2). Anal. Calcd: C, 56.21; H, 5.70. Found: C, 56.5; H, 5.8.

Data Collection and Reduction. Crystal data and intensity collection and structure refinement parameters are summarized in Table I. Colorless crystals of $C_8H_{22}B_{10}O_2S_2$ (III) and $C_{10}H_{25}B_9NaO_3S_2$ (VI) were obtained by slow evaporation of the respective compounds in ethyl ether and ethanol solutions, respectively. Diffraction experiments were performed with an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromated Mo Kα radiation. The molecular structure of compound III was solved by Patterson methods using the automated fragment search program ROTSEARCH/87.[9] The Patterson search was performed by using the two exocluster sulfur atoms of one molecule as an input model. The S–S distance was obtained from ref 4b. Since the structure contains two symmetry-independent molecules in the unit cell, the Patterson search was performed in three steps, i.e. a two-dimensional rotation search followed by two three-dimensional translation searches. A F_0 synthesis with all the S atoms used as a phasing model developed the rest of the structure. The molecular structure of compound V was solved by direct methods using the Multan crystallographic program.[10] The positions of the H atoms bonded to the B atoms were found in a difference Fourier map. The positions of the remaining H atoms were calculated. The positional parameters were fixed, and a global isotropic temperature factor for all H atoms was refined. Least-squares convergence using the Shelx program[11] gave $R = 0.042$ and $R_w = 0.046$ for III and $R = 0.063$ and $R_w = 0.069$ for VI. Scattering factors were taken from ref 12. All drawings were obtained with the PLUTO graphics program.[13]

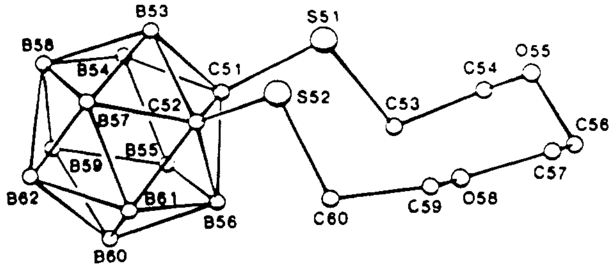

Figure 1. Molecular structure and atom-numbering scheme for 1,2-(1,10-dithia-4,7-dioxadecane-1,10-diyl)-1,2-dicarba-*closo*-dodecaborane (III).

Results and Discussion

Synthesis and Characterization. The reaction of sodium *o*-carborane-1,2-dithiolate with 1,2-bis(2-chloroethoxy)ethane in ethanol, under high dilution conditions, yielded 1,2-(1,10-dithia-4,7-dioxadecane-1,10-diyl)-1,2-dicarba-*closo*-dodecaborane, and sodium 7,8-(1,10-dithia-4,7-dioxadecane-1,10-diyl)-7,8-dicarbaundecaborate(12) (eq 1). The addition of tri- or tetramethylammonium chloride to an aqueous solution of IIIa permitted an easy isolation of the corresponding salt (eq 2).

$$\underset{\text{II}}{o\text{-}HSCB_{10}H_{10}CSH} \xrightarrow[\substack{ClCH_2(CH_2OCH_2)_2CH_2Cl \\ \text{EtOH, high dilution}}]{\text{NaOH}} \underset{\text{III}}{1,2\text{-}SCB_{10}H_{10}CSCH_2(CH_2OCH_2)_2CH_2} + \underset{\text{IIIa}}{Na[7,8\text{-}SCB_9H_{10}CSCH_2(CH_2OCH_2)_2CH_2]} \quad (1)$$

$$\text{IIIa} + HNMe_3Cl \xrightarrow{H_2O} \underset{\text{IV}}{[HNMe_3][7,8\text{-}SCB_9H_{10}CSCH_2(CH_2OCH_2)_2CH_2]} \quad (2)$$

A ν(B–H) stretching frequency near 2550 cm^{-1} was observed for the partially degraded compound IV, while III displayed this frequency near 2580 cm^{-1}. The ^{1}H and ^{13}C NMR spectra were in agreement with the proposed formulas. An X-ray crystal structural determination of III indicated that the molecule consists of a macrocycle where one of its fragments is the 1,2-dicarbaundecaborane moiety. The cluster connection to the ring is through the carbons, as shown in Figure 1. The icosahedra form wavy hexagonal close-packed layers normal to the a axis, while the macrocycle rings fill the interlayer space. The periodicity of the corrugation is along b, and the distance between layers is 9.625 Å. The distances from the center of one icosahedron to those of the next six neigbors in the same layer are 7.98, 7.98, 7.02, 6.88, 6.81, and 7.26 Å, (mean value 7.3 (5) Å). The two shortest intermolecular contacts are O(5)···B(56) = 3.48(6) Å and C-(10)···O(55) = 3.28(6) Å.

The reaction of sodium *o*-carborane-1,2-dithiolate with 1,11-dichloro-3,6,9-trioxaundecane in conditions similar to these reported for III and IV yielded sodium 7,8-(1,13-dithia-4,7,10-trioxatridecane-1,13-diyl)-7,8-dicarba-*nido*-undecaborate, which directly precipitated from the reaction mixture (eq 3). The IR, ^{1}H-NMR and ^{13}C-NMR spectra support the proposed formula.

$$o\text{-}HSCB_{10}H_{10}CSH \xrightarrow[\substack{ClCH_2(CH_2OCH_2)_3CH_2Cl \\ \text{EtOH, high dilution}}]{\text{NaOH}} \underset{\text{VI}}{Na[7,8\text{-}SCB_9H_{10}CSCH_2(CH_2OCH_2)_3CH_2]} \quad (3)$$

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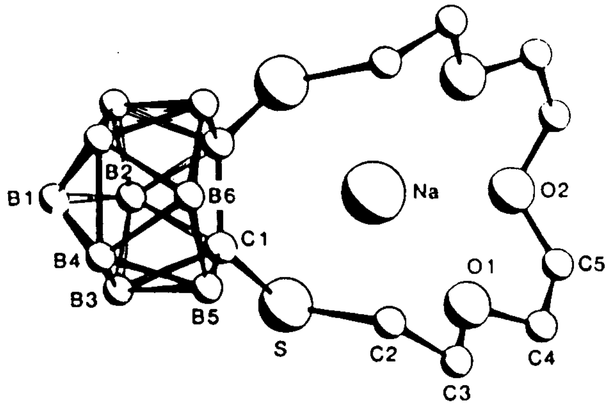

Figure 2. Molecular structure and atom-numbering scheme for sodium 7,8-(1,13-dithia-4,7,10-trioxatridecane-1,13-diyl)-7,8-dicarba-*nido*-undecaborate(12) (VI).

Table II. Final Positional Parameters for Non-Hydrogen Atoms and Equivalent Temperature Factors (Å^2) with Esd's in Parentheses for the $B_{10}C_8H_{22}O_2S_2$ Molecule

atom	*x/a*	*y/b*	*z/c*	B_{eq}
		Molecule 0		
S(1)	0.2257 (1)	0.3128 (0)	0.7850 (2)	4.6
S(2)	0.0960 (1)	0.1963 (1)	0.9995 (2)	4.6
C(1)	0.3462 (3)	0.2643 (2)	0.8897 (3)	3.4
C(2)	0.2771 (3)	0.2015 (2)	1.0077 (3)	3.6
B(3)	0.3414 (3)	0.2651 (2)	1.1057 (4)	3.9
B(4)	0.4899 (3)	0.2907 (2)	1.0086 (4)	4.2
B(5)	0.5022 (3)	0.2426 (2)	0.8323 (4)	4.3
B(6)	0.3598 (3)	0.1908 (2)	0.8275 (4)	3.5
B(7)	0.3803 (3)	0.1931 (2)	1.1897 (4)	4.2
B(8)	0.5131 (4)	0.2466 (2)	1.1924 (4)	4.6
B(9)	0.6101 (3)	0.2307 (2)	1.0221 (4)	4.7
B(10)	0.5312 (3)	0.1695 (2)	0.9079 (4)	4.4
B(11)	0.3901 (3)	0.1452 (2)	1.0145 (4)	4.3
B(12)	0.5438 (3)	0.1719 (2)	1.1322 (4)	4.6
C(3)	0.2183 (4)	0.2917 (3)	0.5643 (4)	6.1
C(4)	0.1067 (4)	0.3272 (3)	0.4730 (4)	8.8
O(5)	−0.0259 (3)	0.3104 (2)	0.5091 (4)	7.7
C(6)	−0.1062 (4)	0.2627 (3)	0.4314 (4)	9.0
C(7)	−0.1569 (4)	0.2209 (3)	0.5565 (4)	7.8
O(8)	−0.0483 (3)	0.1862 (2)	0.6265 (3)	7.4
C(9)	−0.0842 (3)	0.1474 (3)	0.7573 (4)	6.6
C(10)	0.0477 (3)	0.1325 (2)	0.8649 (4)	4.9
		Molecule 50		
S(51)	0.1590 (1)	0.0601 (1)	0.3278 (2)	4.9
S(52)	0.2765 (11)	−0.0595 (1)	0.1149 (1)	4.8
C(51)	0.2750 (3)	0.0110 (2)	0.4410 (3)	3.7
C(52)	0.3366 (3)	−0.0529 (2)	0.3285 (3)	3.4
B(53)	0.4363 (3)	0.0100 (2)	0.3694 (4)	3.9
B(54)	0.4105 (3)	0.0378 (2)	0.5765 (4)	4.5
B(55)	0.2762 (4)	−0.0073 (3)	0.6465 (4)	4.6
B(56)	0.2272 (3)	−0.0611 (2)	0.4856 (4)	3.5
B(57)	0.5071 (3)	−0.0633 (2)	0.3970 (4)	4.2
B(58)	0.5523 (4)	−0.0092 (3)	0.5490 (4)	4.7
B(59)	0.4525 (4)	−0.0208 (3)	0.7212 (4)	5.0
B(60)	0.3379 (3)	−0.0812 (2)	0.6672 (4)	4.3
B(61)	0.3743 (3)	−0.1086 (2)	0.4663 (4)	3.9
B(62)	0.5116 (4)	−0.0825 (2)	0.6122 (4)	4.5
C(53)	−0.0096 (3)	0.0408 (2)	0.3901 (4)	5.6
C(54)	−0.1164 (4)	0.0774 (3)	0.2911 (4)	6.8
O(55)	−0.1383 (3)	0.0606 (2)	0.1193 (3)	6.1
C(56)	−0.2265 (4)	0.0133 (3)	0.0810 (4)	8.1
C(57)	−0.1598 (4)	−0.0319 (3)	−0.0263 (4)	8.1
O(58)	−0.0498 (3)	−0.0596 (2)	0.0782 (3)	6.1
C(59)	0.0233 (4)	−0.1031 (3)	−0.0098 (4)	6.2
C(60)	0.1525 (3)	−0.1213 (2)	0.1027 (4)	4.9

Table III. Final Positional Parameters for Non-Hydrogen Atoms and Equivalent Temperature Factors (Å^2) with Esd's in Parentheses for the $Na[B_9C_{10}H_{25}O_3S_2]$ Compound

atom	*x/a*	*y/b*	*z/c*	B_{eq}
S	0.5928 (1)	0.1283 (1)	0.6048 (1)	3.7
Na	0.4651 (1)	0.2500 (0)	0.4554 (3)	3.7
B(1)	0.7074 (4)	0.2500 (0)	0.9933 (7)	4.0
B(2)	0.6254 (4)	0.2500 (0)	0.8603 (7)	3.9
B(3)	0.6896 (3)	0.1471 (4)	0.8864 (5)	4.0
B(4)	0.7951 (3)	0.1846 (4)	0.9146 (5)	3.8
B(5)	0.7650 (3)	0.1488 (4)	0.7346 (5)	3.9
B(6)	0.8358 (4)	0.2500 (0)	0.7621 (8)	4.1
C(1)	0.6703 (2)	0.1924 (3)	0.7108 (4)	3.0
C(2)	0.6489 (3)	0.1072 (3)	0.4329 (5)	4.1
C(3)	0.5893 (3)	0.0629 (3)	0.3214 (5)	4.5
C(4)	0.4670 (3)	0.1001 (4)	0.1789 (5)	5.1
C(5)	0.4046 (6)	0.1676 (8)	0.1494 (9)	16.2
O(1)	0.5179 (2)	0.1245 (2)	0.3017 (3)	4.7
O(2)	0.3904 (3)	0.2500 (0)	0.2240 (3)	4.1

Table IV. Bond Lengths (Å) with Esd's in Parentheses for the $B_{10}C_8H_{22}O_2S_2$ Molecule

	molecule 0	molecule 50
C(1)–C(2)	1.858 (5)	1.826 (5)
C(1)–B(3)	1.730 (4)	1.720 (4)
C(1)–B(4)	1.703 (4)	1.716 (4)
C(1)–B(5)	1.696 (4)	1.690 (4)
C(1)–B(6)	1.729 (6)	1.730 (6)
C(2)–B(3)	1.711 (6)	1.721 (6)
C(2)–B(6)	1.736 (4)	1.736 (4)
C(2)–B(7)	1.683 (4)	1.698 (4)
C(2)–B(11)	1.668 (6)	1.679 (5)
B(3)–B(4)	1.799 (5)	1.809 (5)
B(3)–B(7)	1.773 (7)	1.786 (7)
B(3)–B(8)	1.780 (5)	1.777 (4)
B(4)–B(5)	1.786 (5)	1.785 (6)
B(4)–B(8)	1.763 (5)	1.763 (6)
B(4)–B(9)	1.773 (6)	1.767 (6)
B(5)–B(6)	1.799 (6)	1.788 (6)
B(5)–B(9)	1.766 (4)	1.772 (5)
B(5)–B(10)	1.758 (7)	1.761 (7)
B(6)–B(10)	1.779 (5)	1.765 (4)
B(6)–B(11)	1.808 (5)	1.799 (5)
B(7)–B(8)	1.757 (6)	1.739 (6)
B(7)–B(11)	1.775 (5)	1.773 (5)
B(7)–B(12)	1.760 (5)	1.767 (4)
B(8)–B(9)	1.769 (5)	1.782 (5)
B(8)–B(12)	1.777 (7)	1.776 (7)
B(9)–B(10)	1.774 (6)	1.774 (6)
B(9)–B(12)	1.746 (6)	1.763 (7)
B(10)–B(11)	1.772 (5)	1.788 (5)
B(10)–B(12)	1.782 (4)	1.784 (5)
B(11)–B(12)	1.776 (5)	1.770 (5)
S(1)–C(1)	1.742 (4)	1.752 (4)
S(1)–C(3)	1.818 (3)	1.809 (3)
S(2)–C(2)	1.752 (3)	1.748 (3)
S(2)–C(10)	1.820 (4)	1.828 (4)
C(3)–C(4)	1.471 (6)	1.480 (5)
C(4)–O(5)	1.397 (5)	1.416 (4)
O(5)–C(6)	1.425 (6)	1.376 (6)
C(6)–C(7)	1.491 (6)	1.516 (7)
C(7)–O(8)	1.377 (5)	1.423 (5)
O(8)–C(9)	1.430 (6)	1.432 (6)
C(9)–C(10)	1.498 (4)	1.515 (5)

An X-ray crystal structural determination of VI showed the molecule to be composed of a carborane cluster, where the two carbons are externally connected via an organic chain, as shown in Figure 2. The negative charge of the 7,8-dicarba-*nido*-undecaborate moiety is counterbalanced by the sodium cation, which is connected to the macrocycle via the three oxygen and the two sulfur atoms. The ion is not placed strictly within the cavity but slightly outward, being in a trans position with respect to the cluster's vacancy.

The arrangement of the icosahedra and the Na$^+$ ions in the crystal can be described by a distorted *A* lattice complex[14] defined by the cell transformation $a' = a/2$, $b' = b$, $c' = c$. The center of the icosahedron is at approximately 0,0,0 and the Na$^+$ is at approximately $^1/_2$, 0, $^1/_2$.

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[14] Hermann, C. *Z. Kristallogr.* **1960**, *113*, 142.

Table V. Selected Bond Angles (deg) with Esd's in Parentheses for the $B_{10}C_9H_{22}O_2S_2$ Molecule

	molecule 0	molecule 50		molecule 0	molecule 50
S(1)–C(1)–C(2)	117.2 (2)	117.7 (2)	C(4)–O(5)–C(6)	125.7 (4)	116.4 (3)
S(1)–C(1)–B(3)	112.5 (2)	113.0 (2)	O(5)–C(6)–C(7)	112.6 (3)	110.4 (3)
S(1)–C(1)–B(4)	121.0 (3)	120.7 (3)	C(6)–C(7)–O(8)	109.6 (3)	107.4 (3)
S(1)–C(1)–B(5)	128.3 (2)	126.2 (2)	C(7)–O(8)–C(9)	113.9 (3)	112.8 (3)
S(1)–C(1)–B(6)	121.7 (2)	121.5 (2)	O(8)–C(9)–C(10)	107.2 (3)	108.2 (3)
C(1)–S(1)–C(3)	104.9 (2)	104.8 (2)	C(9)–C(10)–S(2)	108.2 (3)	108.9 (3)
S(1)–C(3)–C(4)	106.8 (3)	108.7 (3)	C(10)–S(2)–C(2)	105.5 (2)	105.3 (2)
C(3)–C(4)–O(5)	113.2 (4)	113.2 (4)			

Average Bond Angles (deg)

	around all triangular faces			around all pentagonal rings		
angle type	no.	molecule 0	molecule 50	no.	molecule 0	molecule 50
C–C–B	4	57.5 (5)	58.1 (2)	4	107.9 (6)	108.4 (4)
C–B–C	2	65.1 (4)	63.9 (4)	0		
B–C–B	6	63.5 (4)	63.3 (3)	2	108.2 (4)	109.1 (3)
				4	114.1 (7)	113.9 (3)
C–B–B	12	58.2 (9)	58.4 (9)	16	106.5 (18)	106.3 (15)
B–B–B	36	60.0 (6)	60.0 (7)	34	107.9 (10)	108.0 (10)
	60 tot.			60 tot.		

Table VI. Bond Lengths (Å) with Esd's in Parentheses for the $Na[B_9C_{10}H_{25}O_3S_2]$ Compound

C(1)–C(1)′	1.596 (8)	B(4)–B(4)′	1.812 (7)
C(1)–B(2)	1.723 (7)	B(5)–B(6)	1.803 (7)
C(1)–B(3)	1.739 (6)	S–C(1)	1.781 (4)
C(1)–B(5)	1.612 (6)	S–C(2)	1.813 (4)
B(1)–B(2)	1.760 (9)	C(2)–C(3)	1.505 (6)
B(1)–B(3)	1.746 (6)	C(3)–O(1)	1.415 (5)
B(1)–B(4)	1.791 (7)	C(4)–C(5)	1.376 (7)
B(2)–B(3)	1.759 (6)	C(4)–O(1)	1.410 (5)
B(3)–B(4)	1.746 (6)	C(5)–O(2)	1.345 (7)
B(3)–B(5)	1.812 (7)	Na–S	2.942 (2)
B(4)–B(5)	1.771 (6)	Na–O(1)	2.377 (3)
B(4)–B(6)	1.772 (7)	Na–O(2)	2.403 (4)

The general conformation of the macrocyclic ring in both molecules, III and VI, is roughly the same. The most significant differences are in the C(6)–O(5)–C(14) angle (125.7 (4) and 116.0 (3)°), and in the torsional angle C(7)–O(8)–C(9)–C(10) (−157.4 and −169.7°). Final atomic parameters for non-hydrogen atoms are reported in Tables II and III. Selected distances and bond angles are reported in Tables IV–VII.

One of the main features of both molecular structures III and VI is the spatial disposition of the macrocyclic chain, which goes outward from the cluster without presenting a folding tendency such as that presented by similar derivatives of 2,5-bis(methylthio)pyridine.[15a,b] Molecular mechanic calculations have shown that the folding tendency of the pyridine based macrocycle is present even in the free ligand and this is corroborated by the molecular structure of the 15-aza-6-oxa-3,9-dithiabicyclo-[9.3.1]pentadeca-1(15),11,13-triene.[15c]

Table VII. Selected Bond Angles (deg) with Esd's in Parentheses for the $Na[B_9C_{10}H_{25}O_3S_2]$ Compound

S–C(1)–C(1)′	119.9 (2)	C(4)–C(5)–O(2)	126.5 (5)
S–C(1)–B(2)	112.3 (3)	C(5)–O(2)–C(5)′	116.0 (6)
S–C(1)–B(3)	115.6 (3)	S–Na–O(1)	67.4 (1)
S–C(1)–B(5)	120.6 (3)	O(1)–Na–O(2)	69.8 (1)
C(1)–S–C(2)	105.2 (2)	S–Na–O(2)	137.1 (1)
S–C(2)–C(3)	110.2 (3)	S–Na–S	69.9 (1)
C(2)–C(3)–O(1)	109.0 (3)	O(1)–Na–O(1)	94.0 (1)
O(1)–C(4)–C(5)	113.0 (4)		

To test the reactivity of this type of macrocycles, the reaction of $Na[7,8\text{-}SCB_9H_{10}CSCH_2(CH_2OCH_2)_3CH_2]$ with Wilkinson's catalyst in ethanol was carried out, yielding $(PPh_3)_2RhH[7,8\text{-}SCB_9H_9CSCH_2(CH_2OCH_2)_3CH_2]$ as indicated in eq 4

$$Na[7,8\text{-}SCB_9H_{10}CSCH_2(CH_2OCH_2)_3CH_2] + RhCl\,(PPh_3)_3 \xrightarrow[\text{ethanol}]{} (PPh_3)_2RhH[7,8\text{-}SCB_9H_9CSCH_2(CH_2OCH_2)_3CH_2] + NaCl + PPh_3 \quad (4)$$

VII

Elemental analysis, IR data, and the visible spectrum suggest this formulation. Good-quality crystals were obtained from an acetone solution; however, we have not been able, at present, to stabilize the crystal due to the loss of solvent molecules. Work is under way to overcome this difficulty.

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Registry No. III, 122924-04-3; IIIa, 122924-05-4; IV, 122924-09-8; V, 122924-07-6; VI, 122967-19-5; VII, 122967-20-8; 1,2-bis(2-chloroethoxy)ethane, 112-26-5; *o*-carborane-1,2-dithiol, 23810-63-1; 1,11-dichloro-3,6,9-trioxoundecane, 638-56-2; $RhCl(PPh_3)_3$, 14694-95-2.

Supplementary Material Available: Listings of final positional parameters for hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, bond angles, torsion angles of the macrocyclic rings, and bond lengths for hydrogen atoms for both molecules (12 pages); listings of observed and calculated structure factors for both molecules (22 pages). Ordering information is given on any current masthead page.

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