# Macrocycles incorporating *closo*- and *nido*-Carbaborane Cages: Molecular Structure of 1,2-(3'-oxapentane-1',5'-dithiolato-*SS'*)-1',2'-dicarba-*closo*-dodecaborane†

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Reaction of 1,2-dimercapto-1,2-dicarba-*closo*-dodecaborane under basic conditions with appropriate dihalogenated organic compounds results in the formation of macrocycles incorporating 7,8-dicarbaundecaborate or 1,2-dicarba-*closo*-dodecaborane units. Polymers are obviated by using high dilution. The crystal structure of 1,2-(3'-oxapentane-1',5'-dithiolato-*SS'*)-1',2'-dicarba-*closo*-dodecaborane has been determined. It crystallizes in space group $P2_1/a$ with four formula units in a cell of dimensions $a$ = 11.708(2), $b$ = 10.209(3), $c$ = 12.613(3) Å, and $\beta$ = 109.04(2)°.

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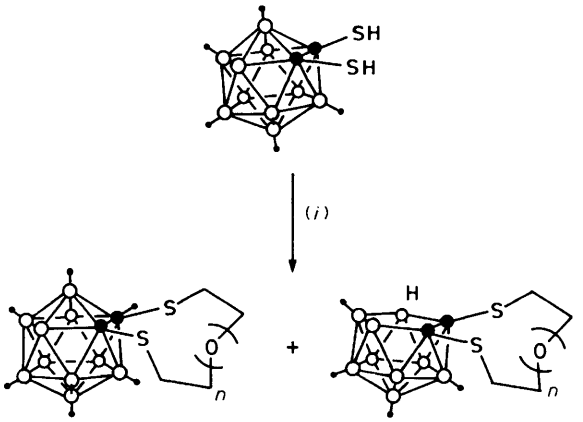
Numerous macrocyclic as well as macropolycyclic ligands containing sulphur binding sites have been synthesized in recent years and shown to complex various transition-metal cations.[1–6] On the other hand the complex chemistry of the decahydro-7,8-dicarbaundecaborate derivatives is well known and documented, especially due to Hawthorne and co-workers.[7–10] However, the co-operative effect that may be present in a compound containing both types of subunits has not been observed. To gain insight into this possible phenomenon we have synthesized several potentially polynucleating ligands, basically constituted by the 7,8-dicarbaundecaborate or 1,2-dicarba-*closo*-dodecaborane units and a sulphur-containing macrocycle (Scheme). In subsequent reports, the reactivity of these ligands towards transition-metal ions will be reported.



**Scheme.** (*i*) (*a*) KOH, (*b*) $Cl(CH_2CH_2O)_nCH_2CH_2Cl$, in ethanol

## Experimental

Before use 1,2-dicarba-*closo*-dodecaborane (Dexsil Chemical Corporation) was sublimed. 1,2-Dimercapto-1,2-dicarba-*closo*-dodecaborane (**1**) was prepared from $C_2B_{10}H_{12}$ according to the literature.[11] All other reagents were Fluka or Aldrich and were used as supplied.

Elemental analyses were performed in our analytical laboratory using a Perkin-Elmer 240-B microanalyser. The $^1H$ n.m.r. spectra were obtained by using a Bruker AM 400WB, i.r. spectra of KBr pellets using a Perkin-Elmer 240FT spectrophotometer.

*Preparations.—Sodium* 7,8-(3',6'-*dioxaoctane*-1',8'-*dithiolato*-SS')-7,8-*dicarbaundecaborate dihydrate* (**2**). The synthesis is analogous to the preparation of the tetramethylammonium salt,[12] except for the separation process.

Concentration by rotary evaporation of the water layer resulted in the isolation of a white solid, which was filtered off, washed with water, and diethyl ether (yield 930 mg, 59%). I.r. (KBr): ν(O–H) 3 627; ν(C–H) 2 921, 2 882; ν(B–H) 2 537, 2 521; ν(C–O) 1 115 and 1 081 cm$^{-1}$. $^1H$ N.m.r.: δ 3.7 (m, 8, $OCH_2$) and 3.0 (m, 8, $SCH_2$, $H_2O$).

*Trimethylammonium* 7,8-(3'-*oxapentane*-1',5'-*dithiolato*-SS')-7,8-*dicarba*-nido-*undecaborate* (**3**) *and* 1,2-(3'-*oxapentane*-1',5'-*dithiolato*-SS')-1,2-*dicarba*-closo-*dodecaborane* (**4**). Under a dinitrogen atmosphere, bis-(2-chloroethyl) ether (1.03 g, 7.2 mmol) was dissolved in degassed absolute ethanol (40 cm$^3$). Sodium hydroxide (0.57 g, 14.4 mmol) and 1,2-dimercapto-1,2-dicarbo-*closo*-dodecaborane (1.5 g, 7.2 mmol) were dissolved in the same solvent (40 cm$^3$). By means of a syringe pump, the dichloride and the carbaborane were added simultaneously from syringes at a rate of 4 cm$^3$ h$^{-1}$ onto refluxing degassed absolute ethanol (250 cm$^3$), contained in a round-bottom flask equipped with three condensers. To permit slow contact of the two reacting solutions, the syringe tubes discharged into lateral condensers. After the elimination of NaCl, the filtrate was evaporated and water (50 cm$^3$) and diethyl ether (50 cm$^3$) were added. The water layer was washed with more ether. Trimethylammonium chloride (excess) was added to the aqueous phase, resulting in the formation of a white precipitate. This was filtered off, washed with water and ether, and dried in vacuum. Yield of compound (**3**) 0.5 g (21%) (Found: C, 32.65; H, 8.35; N, 4.15. Calc.: C, 33.00; H, 8.55; N, 4.25%). I.r. (KBr): ν(B–H) 2 528; ν(C–O–C) 1 112 cm$^{-1}$. N.m.r. [$(CD_3)_2CO$]: $^1H$, δ 3.75 (m, 2, OCH), 3.5 (m, 2, OCH); 3.27 (m, 2, SCH), 3.18 [s, 9, $N(CH_3)_3H$], and 2.73 (m, 2, SCH); $^{13}C$, δ 70.0 ($OCH_2$), 46.5 ($NCH_3$), and 39.6 p.p.m. ($SCH_2$).

The combined ether fractions were washed with a water–NaOH solution, discarding the aqueous phase. The ether

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

solution was dried (anhydrous $Na_2SO_4$, 24 h) and evaporated to yield a yellowish oil. This was chromatographed on alumina using diethyl ether as the eluant. The solution was evaporated and the oily product chromatographed as before. After partial evaporation of the solvent and on standing, white crystals of compound (**4**) appeared. Yield 0.44 g (22%) (Found: C, 26.4; H, 6.45. Calc.: C, 25.9; H, 6.45%). I.r. (KBr): ν(B–H) 2 597, 2 574, and 2 544; ν(C–O–C) 1 142 $cm^{-1}$. Mass spectrum: $m/z$ 278 ($M$), 250 [$M - (CH_2CH_2)$], and 235 [$M + 1 - (CH_2CH_2O)$].

*Tetramethylammonium* 7,8-(3′,6′,9′-*trioxaundecane*-1′,11′-*dithiolato*-SS′)-7,8-*dicarbaundecaborate* (**5**). The synthesis was analogous to that of the sodium salt, previously described,[12] except that $NMe_4OH$ was used instead of NaOH. I.r. (KBr): ν(B–H) 2 520; ν(C–O–C) 1 117 $cm^{-1}$. $^{13}C$ N.m.r. [$(CD_3)_2CO$]: δ 71.8 ($CH_2O$), 70.7 ($CH_2O$), 70.4 ($CH_2O$), and 37.4 p.p.m. ($CH_2S$).

*Bis*(2-*chloroethyl*)*tosylamine* (**6**). Under a dinitrogen atmosphere, bis(2-chloroethyl)amine hydrochloride (9.107 g, 0.05 mol) was slowly added (1 h) to a warm solution (40 °C) of toluene-*p*-sulphonyl chloride (9.525 g, 0.05 mol) (tosyl chloride) in pyridine (100 $cm^3$). After the addition, the reaction mixture was kept at 50—60 °C for 30 min and then cooled. Water (200 $cm^3$) was added and the mixture neutralized with aqueous NaOH. After stirring overnight the mixture was cooled in an ice-bath for a few hours, and the white solid which separated was filtered off, washed with ice-cold 95% ethanol, and dried in vacuum. Yield 11.2 g (74%) (Found: C, 44.35; H, 5.05; N, 4.50. Calc.: C, 44.6; H, 5.05; N, 4.75%).

*Caesium*7,8-(3′-*toluene*-p-*sulphonyl*-3-*azapentane*-1′,5′-*dithiolato*-SS′)-7,8-*dicarba*-nido-*undecaborate* (**7**). The procedure was similar to the synthesis of compounds (**3**) and (**4**). Compound (**6**) (1.42 g, 4.8 mmol) and the sodium salt of compound (**1**) (4.8 mmol) were each dissolved in ethanol (40 $cm^3$). The trimethylammonium salt obtained was redissolved in water–NaOH, and caesium carbonate (excess) was added. Upon neutralization of the solution with diluted aqueous HCl, a pink solid separated which was filtered off, washed with water and ether, and dried in vacuum. Yield 1.42 g (53.4%) (Found: C, 28.95; H, 5.05; N, 2.70. Calc.: C, 28.20; H, 4.50; N, 2.55%). I.r. (KBr): ν(C–H) 2 924; ν(B–H) 2 573; ν(C=C) 1 597 $cm^{-1}$. $^1H$ N.m.r. [$(CD_3)_2CO$]: δ 8—7.3 (m, 4, $C_6H_4$), 3.8—3 (m, 8, $SCH_2CH_2N$), and 2.5 (s, 3, $CH_3$).

*Tetramethylammonium* 7,8-(*propane*-1,3′-*dithiolato*-SS′)-*dicarba*-nido-*undecaborate* (**8**). The synthesis was similar to that of compounds (**3**) and (**4**). 1,3-Dibromopropane (0.34 g, 1.68 mmol) and the sodium salt of compound (**1**) (1.68 mmol) were used. Yield 0.12 g (23%) (Found: C, 33.5; H, 8.90; N, 4.55. Calc.: C, 34.7; H, 8.95; N, 4.5%). I.r. (KBr): ν(B–H) 2 534 $cm^{-1}$. N.m.r. [$(CD_3)_2CO$]: $^1H$, δ 3.47 (s, 12, $NCH_3$), 2.84 (m, 1, SCH), 2.63 (m, 2, SCH), 2.30 (m, 1, SCH), and 1.85 (m, 2, $CCH_2$); $^{13}C$, δ 56.5 ($NCH_3$), 37.6 ($SCH_2$), and 35.49 p.p.m. ($SCH_2CH_2$).

*Tetramethylammonium* 7,8-(*butane*-1′,4′-*dithiolato*-SS′)-7,8-*dicarba*-nido-*undecaborate* (**9**). The synthesis is analogous to the preparation of compound (**3**), 1,4-dibromobutane (1.52 g, 7.2 mmol) and the sodium salt of (**1**) (1.5 g, 7.2 mmol) being used. Yield 0.54 g (23%) (Found: C, 36.5; H, 9.0; N, 4.15. Calc. C, 36.9; H, 9.2; N, 4.3%). I.r. (KBr): ν(B–H) 2 525 $cm^{-1}$. N.m.r. [$(CD_3)_2CO$]: $^1H$, δ 3.45 (s, 12, $NCH_3$), 2.9 (m, 2, SCH), 2.35 (m, 2, SCH), 1.9 (m, 2, CCH), and 1.55 (m, 2, CCH); $^{13}C$, δ 56 ($NCH_3$), 39.2 ($SCH_2$), and 29.4 p.p.m. ($SCH_2CH_2$).

1,2-(*Pentane*-1,5-*dithiolato*-SS′)-1,2-*dicarba*-closo-*dodecaborane* (**10**). A polymer with this formulation was directly precipitated when 1,5-dibromopentane (0.77 g, 3.36 mmol) and the sodium salt of (**1**) (3.36 mmol) were mixed under conditions similar to those described before. Yield 0.32 g (34.5%). (Found: C, 30.5; H, 7.30. Calc.: C, 30.45; H, 7.25%). I.r. (KBr): ν(B–H) 2 564 $cm^{-1}$.

1,2-(*Butane*-1,4-*dithiolato*-SS′)-1,2-*dicarba*-closo-*dodecaborane* (**11**). A polymer with this formulation was directly precipitated when a solution containing the sodium salt of (**1**) (1.68 mmol) in degassed absolute ethanol (60 $cm^3$) was mixed with 1,4-dibromobutane (0.36 g, 1.68 mmol). The mixture was stirred at room temperature for 20 h yielding a solid, which was washed with water and ethanol, and dried in vacuum. Yield 0.15 g (34.3%). (Found: C, 27.0; H, 6.60. Calc.: C, 27.5; H, 6.85%). I.r. (KBr): ν(B–H) 2 590—2 570 $cm^{-1}$.

The ethanol was eliminated by rotary evaporation and the mixture treated as for compound (**3**). Only 12 mg of the degraded species, (**9**) was obtained.

1,1′-*Ethylenebis*(1,2-*dicarba*-closo-*dodecaborane*) (**12**). To a three-neck flask (250 $cm^3$) fitted with a reflux condenser having a gas inlet-outlet was added $C_2B_{10}H_{12}$ (1 g, 6.94 mmol) and dry benzene (40 $cm^3$). The solution was heated to reflux and a 1.6 mol $dm^{-3}$ solution of butyl-lithium in hexane (2.5 $cm^3$) was added dropwise over 0.5 h. The solution was kept at reflux for 1 h and 1,2-dibromoethane (2.24 $cm^3$, 2.6 mmol) was added slowly. After approximately 30 h of reflux, the reaction mixture was cooled and aqueous 4 mol $dm^{-3}$ HCl (30 $cm^3$) was added dropwise. The mixture was vigorously stirred for 10 min and the two layers separated. The benzene solution was dried over anhydrous magnesium sulphate and evaporated in a rotatory evaporator to yield a white solid. This was recrystallized from hexane. Yield 0.55 g (55%). (Found: C, 22.45; H, 8.70. Calc.: C, 22.90, H, 8.30%). I.r. (KBr): ν(C–H, carborane), 3 071; ν(B–H), 2 601 $cm^{-1}$. N.m.r. ($CDCl_3$): $^1H$, δ 2.85 (s, 2, $CH_2$) and 3.53 (s, 1, CH of carborane); $^{13}C$, δ 35.52 ($CH_2$) and 54.48 p.p.m. (C of carborane).

*Tetramethylammonium* 7,7′-*ethylenebis*(7,8-*dicarba*-nido-*undecaborate*)*dihydrate* (**13**). To a three-neck flask equipped with a reflux condenser having a gas inlet-outlet connected to a nitrogen manifold was added compound (**12**) (1 g, 3.18 mmol) and KOH (0.54 g, 9.54 mmol) in degassed absolute ethanol (30 $cm^3$). After 4 h of reflux the reaction mixture was cooled and water (30 $cm^3$) and tetramethylammonium chloride (excess) were added. The white precipitate formed was filtered off and recrystallized from ethanol–water. Yield 0.85 g (85%). (Found: C, 35.05; H, 11.05; N, 5.50. Calc.: 35.25; H, 11.35; N, 5.85%). I.r. (KBr): ν(C–H) 3 031; ν(B–H) 2 516 $cm^{-1}$. $^1H$ N.m.r. [$(CD_3)_2CO$]: δ 2.8 (s, 2, $CH_2$), 3.4 [s, 12, $N(CH_3)_3$], and 3.9 (s, 1 CH of carborane).

2,2′-*Ethylenebis*(1-*mercapto*-1,2-*dicarba*-closo-*dodecaborane*) (**14**). To a three-neck flask equipped with a gas inlet-outlet connected to a nitrogen manifold and containing dry diethyl ether (30 $cm^3$) was added compound (**12**) (1 g, 3.18 mmol) and butyl-lithium (4 $cm^3$, 6.5 mmol). After 30 min, sulphur (0.21 g, 6.6 mmol) was added slowly. The ice-bath was removed and the stirring continued for 1 h. The solution was cooled again to 0 °C and aqueous 4 mol $dm^{-3}$ HCl (30 $cm^3$) was added dropwise. The ether layer was dried over anhydrous magnesium sulphate and evaporated in vacuum to yield a solid which was recrystallized in hexane. Yield 0.73 g (73%). (Found: C, 19.05; H, 7.25. Calc.: C, 19.15; H, 6.90%). I.r. (KBr): ν(C–H) 2 969; ν(B–H) 2 601 $cm^{-1}$. N.m.r. ($CDCl_3$): $^1H$, δ 2.8 (s, 2 $CH_2$), and 3.77 (s, 1, SH); $^{13}C$, δ 35.47 ($CH_2$), 77.64 (CSH), and 79.76 p.p.m. ($C^2$).

*Crystallography.*—Colourless crystals of compound (**4**) ($C_6H_{18}B_{10}OS_2$) were grown from an ether solution of the compound.

*Crystal data.* $M$ 278.43, space group $P2_1/a$, $a = 11.708(2)$, $b = 10.209(3)$, $c = 12.613(3)$ Å, $\beta = 109.04(2)°$, $U = 1\,425(1)$ Å$^3$, $Z = 4$, $D_c = 1.30$ g $cm^{-3}$, $F(000) = 576$, $\lambda(Mo\text{-}K_\alpha) = 0.710\,69$ Å, $\mu = 3.348$ $cm^{-1}$, $T = 291$ K.

Parallelepiped crystal with dimensions 0.23 × 0.31 × 0.28 mm. Lattice parameters refined from 25 reflections in the range

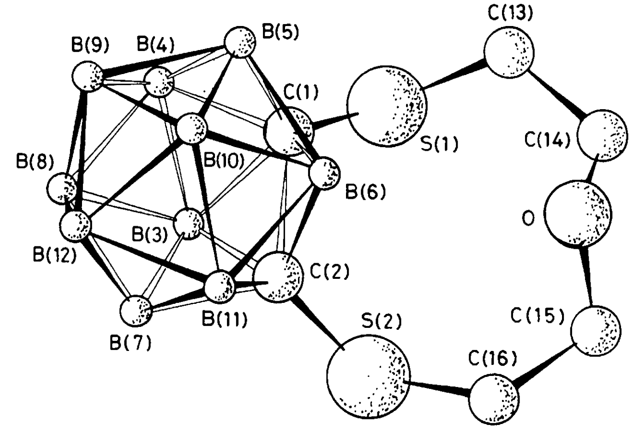

**Figure 1.** Molecular structure and atom numbering scheme for compound (**4**)

$5 < 2\theta < 20°$. Enraf-Nonius CAD-4 diffractometer, Mo-$K_\alpha$ radiation. 2 500 Independent reflections with $(\sin\theta)/\lambda \leqslant 0.595$ Å, $-13 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 12$, $0 \leqslant l \leqslant 15$, 1 130 reflections with $I \geqslant 2.5\sigma(I)$. One standard reflection checked every 50 measurements; no significant deviation.

The crystal structure was determined by multisolution direct methods (20 sets with 150 random phases for each) using the OMEGA88 program[13] based on the omega function procedure.[14] These sets revealed all the non-hydrogen atoms of the structure. The H atoms bound to B were found from $F_o$ synthesis and their positional parameters and a common thermal parameter refined. The remaining H atoms were either placed at the expected positions or found in the $F_o$ syntheses and only a common thermal parameter was refined ($B = 8.6$ Å$^2$). Least-squares refinement using the SHELX76 program[15] gave $R = 0.040$ and $R' = 0.044$ for 1 130 observed reflections (weighting scheme: $w = 1/(\sigma^2 + 0.001\ 869F^2)$. Final $(\Delta/\sigma)_{\text{max.}} = 0.48$. Maximum and minimum heights in final $F_o$ synthesis, 0.21 and $-0.25$ e Å$^{-3}$. Atomic scattering factors from ref. 16.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

## Results and Discussion

*Thioalkylcarborane Macrocycles.*—The reaction of Na$_2$[S$_2$C$_2$B$_{10}$H$_{10}$] with Br(CH$_2$)$_3$Br and Br(CH$_2$)$_4$Br in ethanol, at high dilution, produced white microcrystalline compounds (**8**) and (**9**). When such conditions were not used for Br(CH$_2$)$_4$Br or even when using them for Br(CH$_2$)$_5$Br, polymers (**11**) and (**10**) were obtained. The boron–hydride stretching vibrations of (**8**) and (**9**) appeared as strong i.r. bands near 2 525 cm$^{-1}$ (KBr pellet), while the non-degraded species (**10**) and (**11**) had bands near 2 570 cm$^{-1}$. The $^1$H n.m.r. spectrum of compound (**8**) displayed, in addition to the tetramethylammonium protons, four groups of resonances, with integrations 1:2:1:2, attributed to the methylene hydrogens. This is in agreement with the number of chemically equivalent groups of hydrogens (four) and the number of protons in each group (1:1:2:2). It is worth noting that the proton chemical shifts of the central methylene hydrogens differ by δ 0.54. Such a separation could be explained by considering the spatial disposition of both hydrogens with respect to the cluster's open face. The nearest one would experience a deshielding effect while the other would not. The number and position of the carbon signals are in agreement with the proposed formulae. No $^{13}$C n.m.r. signals attributable to the carborane carbons were found under the conditions used to run these spectra.

**Table 1.** Final positional parameters (× 10$^4$) for non-hydrogen atoms of compound (**4**) with estimated standard deviations (e.s.d.s) in parentheses

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|
| S(1) | 7 070(1) | 1 596(1) | 5 677(1) |
| S(2) | 9 446(1) | 1 690(1) | 8 210(1) |
| O | 7 198(3) | 3 697(4) | 7 609(3) |
| C(1) | 7 112(4) | 389(4) | 6 690(4) |
| C(2) | 8 350(4) | 445(4) | 8 009(4) |
| B(3) | 8 372(5) | −588(5) | 6 941(5) |
| B(4) | 6 876(5) | −1 192(6) | 6 259(5) |
| B(5) | 5 925(5) | −367(6) | 6 892(5) |
| B(6) | 6 872(5) | 718(5) | 7 948(4) |
| B(7) | 8 832(5) | −1 123(6) | 8 365(5) |
| B(8) | 7 933(5) | −2 137(6) | 7 292(5) |
| B(9) | 6 417(6) | −2 007(6) | 7 289(5) |
| B(10) | 6 400(5) | −816(6) | 8 331(5) |
| B(11) | 7 906(5) | −284(6) | 9 019(5) |
| B(12) | 7 617(6) | −1 941(6) | 8 581(5) |
| C(13) | 6 065(5) | 2 886(5) | 5 811(5) |
| C(14) | 6 702(5) | 4 068(5) | 6 459(5) |
| C(15) | 8 381(5) | 4 129(5) | 8 238(5) |
| C(16) | 9 021(5) | 2 993(5) | 8 975(4) |
| H(3) | 8 959(37) | −328(44) | 6 484(34) |
| H(4) | 6 514(37) | −1 396(42) | 5 378(38) |
| H(5) | 5 044(39) | −94(45) | 6 421(35) |
| H(6) | 6 611(37) | 1 715(41) | 8 094(35) |
| H(7) | 9 735(38) | −1 182(42) | 8 784(36) |
| H(8) | 8 387(36) | −3 057(41) | 7 097(35) |
| H(9) | 5 759(35) | −2 715(45) | 7 030(34) |
| H(10) | 5 742(37) | −811(39) | 8 789(36) |
| H(11) | 8 222(35) | 149(44) | 9 814(35) |
| H(12) | 7 772(37) | −2 752(46) | 9 242(35) |

**Table 2.** Bond lengths (Å) with e.s.d.s in parentheses for compound (**4**)

| | | | |
|---|---|---|---|
| C(1)–C(2) | 1.816(6) | B(9)–B(10) | 1.796(8) |
| C(1)–B(3) | 1.722(7) | B(9)–B(12) | 1.772(9) |
| C(1)–B(4) | 1.697(7) | B(10)–B(11) | 1.777(8) |
| C(1)–B(5) | 1.681(7) | B(10)–B(12) | 1.777(8) |
| C(1)–B(6) | 1.732(6) | B(11)–B(12) | 1.778(8) |
| C(2)–B(3) | 1.717(7) | H(3)–B(3) | 1.07(4) |
| C(2)–B(6) | 1.730(6) | H(4)–B(4) | 1.07(4) |
| C(2)–B(7) | 1.708(7) | H(5)–B(5) | 1.05(4) |
| C(2)–B(11) | 1.697(7) | H(6)–B(6) | 1.10(4) |
| B(3)–B(4) | 1.790(8) | H(7)–B(7) | 1.02(4) |
| B(3)–B(7) | 1.784(8) | H(8)–B(8) | 1.15(4) |
| B(3)–B(8) | 1.763(8) | H(9)–B(9) | 1.03(4) |
| B(4)–B(5) | 1.780(9) | H(10)–B(10) | 1.10(4) |
| B(4)–B(8) | 1.763(8) | H(11)–B(11) | 1.05(4) |
| B(4)–B(9) | 1.768(8) | H(12)–B(12) | 1.15(4) |
| B(5)–B(6) | 1.808(8) | C(1)–S(1) | 1.764(5) |
| B(5)–B(9) | 1.788(8) | S(1)–C(13) | 1.810(5) |
| B(5)–B(10) | 1.776(8) | C(13)–C(14) | 1.511(7) |
| B(6)–B(10) | 1.779(7) | C(14)–O | 1.426(7) |
| B(6)–B(11) | 1.808(8) | O–C(15) | 1.423(6) |
| B(7)–B(8) | 1.755(9) | C(15)–C(16) | 1.522(7) |
| B(7)–B(11) | 1.781(8) | C(16)–S(2) | 1.806(5) |
| B(7)–B(12) | 1.746(8) | S(2)–C(2) | 1.764(5) |
| B(8)–B(9) | 1.779(8) | | |
| B(8)–B(12) | 1.792(8) | | |

*Thio-oxa-alkylcarborane Macrocycles.*—Reactions of Na$_2$[S$_2$C$_2$B$_{10}$H$_{10}$] with (ClCH$_2$CH$_2$)$_2$O or (ClCH$_2$CH$_2$OCH$_2$)$_2$, or of [NMe$_4$]$_2$[S$_2$C$_2$B$_{10}$H$_{10}$] with Cl(CH$_2$CH$_2$O)$_3$CH$_2$CH$_2$Cl in ethanol afforded white microcrystalline compounds (**2**), (**5**), (**3**), or (**4**). For compound (**2**) there are two water molecules per

**Table 3.** Selected bond and torsion angles (°) with e.s.d.s in parentheses for compound (**4**)

| | | | |
|---|---|---|---|
| S(1)–C(1)–C(2) | 117.8(3) | O–C(15)–C(16) | 107.4(4) |
| S(1)–C(1)–B(3) | 111.0(3) | C(15)–C(16)–S(2) | 113.6(4) |
| S(1)–C(1)–B(4) | 117.9(3) | C(16)–S(2)–C(2) | 107.1(2) |
| S(1)–C(1)–B(5) | 127.0(3) | S(2)–C(2)–C(1) | 118.7(3) |
| S(1)–C(1)–B(6) | 123.6(3) | S(2)–C(2)–B(6) | 124.0(3) |
| C(1)–S(1)–C(13) | 107.8(2) | S(2)–C(2)–B(11) | 126.5(3) |
| S(1)–C(13)–C(14) | 114.3(4) | S(2)–C(2)–B(7) | 118.4(3) |
| C(13)–C(14)–O | 107.7(4) | S(2)–C(2)–B(3) | 111.1(3) |
| C(14)–O–C(15) | 119.0(4) | | |

| Average bond angles around: | number | all triangular faces | number | all pentagonal rings |
|---|---|---|---|---|
| C–C–B | 4 | 58.2(2) | 4 | 108.7(6) |
| C–B–C | 2 | 63.5(3) | 0 | — |
| B–C–B | 6 | 63.4(4) | 2 | 109.4(3) |
| | | | +4 | 114.2(5) |
| C–B–B | 12 | 58.3(8) | 16 | 106(2) |
| B–B–B | 36 | 60.0(7) | 34 | 108.0(10) |
| | — | | — | |
| | 60 | | 60 | |

| | | | |
|---|---|---|---|
| C(2)–C(1)–S(1)–C(13) | −96.7 | C(14)–O–C(15)–C(16) | −139.4 |
| C(1)–S(1)–C(13)–C(14) | 99.8 | O–C(15)–C(16)–S(2) | 72.8 |
| S(1)–C(13)–C(14)–O | −70.9 | C(15)–C(16)–S(2)–C(2) | −100.1 |
| C(13)–C(14)–O–C(15) | 138.2 | C(16)–S(2)–C(2)–C(1) | 96.5 |

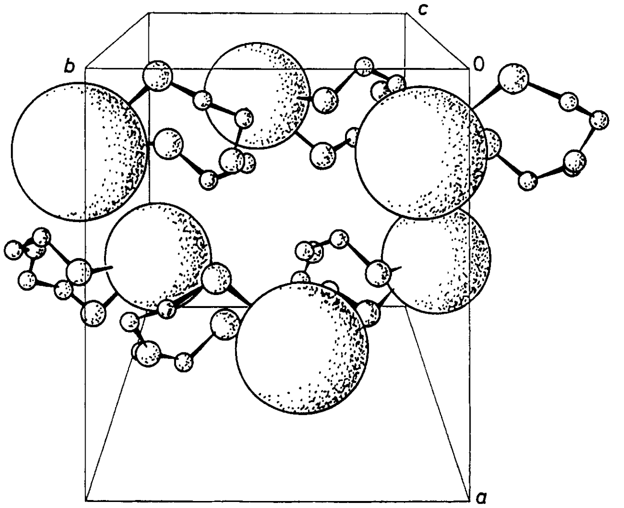

**Figure 2.** Perspective view of the unit cell for compound (**4**)

formula unit. The boron–hydride stretching vibrations of (**2**), (**3**), and (**5**) appeared at 2 540—2 520 cm$^{-1}$ (KBr pellet) and for (**4**) at 2 574 cm$^{-1}$.[1] These frequencies are in accordance with partially degraded or non-degraded formulations. Compound (**2**) (KBr pellets) displays well defined bands in the OH stretching and HOH bending regions, supporting the existence of co-ordinated water molecules. The two well defined bands at 1 610 and 1 600 cm$^{-1}$ suggest that the two molecules are not equally placed in the complex. A thermal gravimetric analysis showed two consecutive weight losses at 399 and 411 K corresponding to two water molecules. The fact that the sodium atom has been found bonded to the $S_2O_3$ unit in somewhat similar molecule, sodium 7,8-(3′,6′,9′-trioxaundecane-1,11′-dithiolato-*SS*′)-7,8-dicarbaundecaborate,[12] suggests co-ordination of water to the metal ion. This is also supported by the fact that the corresponding tetramethylammonium salt (**5**) does not contain any water molecule, as shown by i.r. and elemental analysis.

*Thioaza-alkylcarborane Macrocycles.*—Reaction of $Na_2[S_2C_2B_{10}H_{10}]$ with 2,6-bis(thiomethyl)pyridine or bis(2-chloroethyl)amine under similar conditions to those described for the above mentioned compounds did not yield the expected compounds, however the reaction proceeded as expected when bis(2-chloroethyl)tosylamine was used. Probably, the rigidity of the amine favours a closure mechanism. The $^1H$ n.m.r. spectrum of compound (**6**) displayed alkyl and tosyl resonances at the expected positions.

*Polycarborane Macrocyclic Precursors.*—In order to achieve high molecular recognition through macrocycles containing intricate cavities based on bulky fragments, we have synthesized dicarborane molecules. These are the precursors of molecules similar to those described in the preceding sections, but containing at least two carborane units with non-equivalent arms.

*Bis(carborane) molecules.* The reaction of monolithiated $C_2B_{10}H_{12}$ with 1,2-dibromoethane in benzene followed by addition of acid produced the bis(carborane) (**12**). This compound had already been obtained but by a completely different method.[17] The monosubstitution at CH is supported by the presence in the i.r. spectrum of a C–H (carborane) band at 3 071 cm$^{-1}$. In addition, the $^{13}C$ n.m.r. spectrum displays two signals; one, attributable to the H–C cluster carbon at 54.48 p.p.m. and the other, at 35.5 p.p.m., to $CH_2$. The ν(B–H) at 2 601 cm$^{-1}$ clearly indicates a non-degraded molecule. The corresponding partially degraded molecule (**13**) exhibits ν(B–H) at 2 516 cm$^{-1}$, 85 cm$^{-1}$ lower than for the non-degraded molecule as expected. The $^1H$ and $^{13}C$ n.m.r. spectra of both compounds are in agreement with this formulation.

Reaction of compound (**12**) with butyl-lithium and sulphur followed by protonation yielded (**14**) a two-cluster molecule susceptible to conversion into a macrocycle as for compound (**1**). The existence of the thiol group is corroborated by $^1H$ n.m.r. spectroscopy.

*Crystal Structure.*—One of the problems associated with macrocycles is the possibility of obtaining monoclusters or diclusters (as in this case). To determine the real nature of these macrocycles we decided to solve the molecular structure of compound (**4**). This was chosen because the organic chain was shorter than for the other oxygen-containing members of the series, consequently favouring the dimerization, and because good crystals could be obtained rather easily. A perspective view and atom numbering scheme for compound (**4**) are shown in Figure 1. Final atomic parameters are reported in Table 1, selected distances, bond and torsion angles for the macrocyclic chain in Tables 2 and 3, respectively.

The compound consists of a 1,2-dicarba-*closo*-dodecaborane moiety linked to an exocluster chain which is closed through connection with the cluster carbons. The icosahedral arrangement forms an approximate F lattice and the macrocyclic moieties occupy the octahedral sites. The macrocyclic arrangement can best be explained by considering an alternate sequence of layers normal to [001]. Each of these layers is characterized by having all the macrocycles pointing towards the same direction as shown in Figure 2.

## Acknowledgements

This work was partially supported by a grant no. PB87–0364 from Comisión Intermisterial Para la Ciencia y la Tecnología (Spanish Government).

## References

1 D. Parker, J. M. Lehn, and J. Rimmer, *J. Chem. Soc., Dalton Trans.*, 1985, 1517.

2 J. S. Bradshaw and J. Y. K. Hui, *J. Heterocycl. Chem.*, 1974, **11**, 649.

3 K. P. Balakrishnan, T. A. Kaden, L. Siegfried, and A. D. Zuberbühler, *Helv. Chim. Acta*, 1984, **67**, 1060.

4 H. Fujihara, K. Imaoka, N. Furukawa, and S. Oae, *J. Chem. Soc., Dalton Trans.*, 1986, 465.

5 S. R. Cooper, *J. Am. Chem. Soc.*, 1986, **108**, 1208.

6 S. C. Rawle, J. A. R. Hartman, D. J. Watkin, and S. R. Cooper, *J. Chem. Soc., Chem. Commun.*, 1986, 1083.

7 H. C. Kang, Y. Do, C. B. Knobler, and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1987, **109**, 6530.

8 W. C. Kalb, Z. Demidowicz, D. M. Speckman, C. Knobler, R. G. Teller, and M. F. Hawthorne, *Inorg. Chem.*, 1982, **21**, 4027.

9 J. A. Long, T. B. Marder, and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1984, **106**, 3004.

10 J. A. Walker, L. Zheng, C. B. Knobler, J. Soto, and M. F. Hawthorne, *Inorg. Chem.*, 1987, **26**, 1608.

11 H. D. Smith, jun., C. O. Oberland, and S. Papetti, *Inorg. Chem.*, 1966, **5**, 1013.

12 F. Teixidor, C. Viñas, J. Rius, C. Miravitlles, and J. Casabó, *Inorg. Chem.*, in the press.

13 J. Rius and C. Miravitlles, OMEGA 88, a computer program for solving crystal structures based on the omega function, Institut de Ciencia dels Materials, C.S.I.C., Barcelona, 1988.

14 J. Rius and C. Miravitlles, *Acta Crystallogr., Sect. A*, 1989, **45**, 490.

15 G. M. Sheldrick, SHELX 76, University of Cambridge, 1976.

16 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4 (present distributor, D. Reidel, Dordrecht).

17 L. I. Zakharkin and J. J. Kowle, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1973, **6**, 1428.

*Received* 16*th February* 1989; *Paper* 9/00747D