

New macrocyclic oligoboronates

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Abstract

Two new macrocyclic oligoboronates were prepared in easy one step syntheses from aminodialcohols and phenylboronic acid. Reaction of 2,6-pyridinedimethanol gives a tetrameric species, while 2-(salicylideneamino)-1-hydroxyethane provides a cyclobisboronate. Both compounds are characterized by using X-ray structural analyses. Possible applications in the supramolecular host–guest chemistry are discussed. © 1997 Elsevier Science S.A.

Keywords: Macrocyclic boron complexes; Self-assembly; Host–guest

1. Introduction

In the last few years we have been interested in the synthesis of bicyclic boron compounds derived from diethanolamines [1,2], phenolamines [3,4], iminodiacetic acid [5] and N-alkyl-N-(2-hydroxyethyl)glycine [6], especially in the study of the intramolecular N → B coordination. Bicyclic boron compounds are under investigation with respect to a cytotoxic activity [7–9] and could also have applications in a technique known as boron neutron capture therapy (BNCT) used for the treatment of certain brain tumors [10].

In contrast, the chemistry of macrocyclic oligoboronates has been little studied [11,12], although it can be expected that their hydrolytic stability is increased in comparison to trivalent macrocyclic borates [13].

Neutral macrocyclic receptors containing Lewis acid boron atoms are under investigation as hosts for Lewis bases and anions [14–16]. Even tetracoordinated boronates could be used in this sense, since the dative N → B bond can be broken up by appropriate reagents [17–19].

Recently, the formation of macrocyclic cyclobis-

boronates with incorporated saccharides has gained some attention in the construction of allosteric devices [12].

In comparison to the interesting tetrameric species obtained from dimethyl (1,2,3-triazol-1-yl)borane derivatives [20,21], where the macrocyclic structure is formed by coordinative N → B bonds, macrocyclic oligoboronates are held together by covalent B–O bonds.

In the present contribution a synthetic strategy for the formation of new macrocyclic oligoboronates from aminodialcohols and phenylboronic acid is reported. Thereby the structures of the tetrakisboronate **1** (Scheme 1) and the cyclobisboronate **2** (Scheme 2) have been confirmed by an X-ray structural analysis of single crystals. It is important to note that neither structural type has been reported to date, although they are similar to the macrocyclic boronates cited earlier.

2. Results and discussion

Compound **1** is obtained by the condensation of 2,6-pyridinedimethanol with phenylboronic acid in ethyl acetate (Scheme 1). The quantitative reaction (93% yield) is performed at room temperature and is completed in 15 min. Normally, 2,6-pyridinedimethanol acts as a tridentate monochelating ligand as has been shown in a series of complexes with metal ions and

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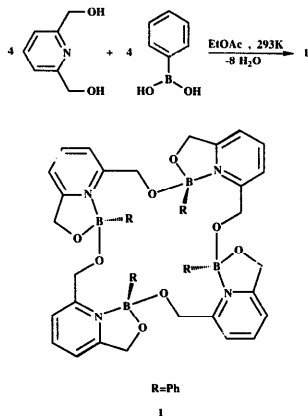
Table 1

Atomic coordinates and isotropic thermal parameters for 1

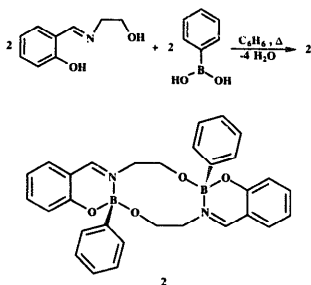
Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U_{eq}</i> (Å ²)
N(1)	0.5175(5)	0.2903(5)	0.3823(5)	0.0647
N(28)	0.4309(5)	0.4507(4)	0.1105(5)	0.0644
N(45)	0.8550(4)	0.5525(5)	0.3807(5)	0.0658
N(59)	0.6606(5)	0.1485(4)	0.1157(4)	0.0608
O(8)	0.4650(5)	0.1111(4)	0.3160(5)	0.0909
O(17)	0.4957(4)	0.4974(4)	0.3140(4)	0.0694
O(25)	0.3117(4)	0.4806(4)	0.1733(5)	0.0845
O(34)	0.7063(4)	0.4996(3)	0.1775(4)	0.0684
O(42)	0.8366(5)	0.6752(4)	0.3156(5)	0.0975
O(51)	0.8075(4)	0.2885(4)	0.3170(4)	0.0668
O(62)	0.8480(4)	0.1869(4)	0.1804(4)	0.0801
O(68)	0.4545(4)	0.1660(3)	0.1803(4)	0.0692
B(9)	0.4328(8)	0.1786(7)	0.2674(8)	0.0716
B(18)	0.4305(8)	0.5213(7)	0.2264(8)	0.0736
B(35)	0.8186(7)	0.5646(7)	0.2639(8)	0.0733
B(52)	0.7859(7)	0.1889(7)	0.2335(7)	0.0666
C(2)	0.5749(7)	0.2750(8)	0.4720(8)	0.0754
C(3)	0.6512(8)	0.3569(9)	0.5798(8)	0.0879
C(4)	0.6716(7)	0.4548(8)	0.5929(7)	0.0904
C(5)	0.6121(6)	0.4698(6)	0.4984(7)	0.0742
C(6)	0.5343(6)	0.3865(6)	0.3937(6)	0.0636
C(7)	0.5422(8)	0.1627(8)	0.4352(9)	0.0966
C(10)	0.3081(7)	0.1725(6)	0.2189(8)	0.0829
C(11)	0.2326(8)	0.1453(8)	0.1088(9)	0.1149
C(12)	0.1261(1)	0.1401(1)	0.0731(1)	0.1587
C(13)	0.0901(1)	0.1562(2)	0.1432(2)	0.1599
C(14)	0.1651(1)	0.1852(2)	0.2502(2)	0.1632
C(15)	0.2713(9)	0.1917(9)	0.2897(9)	0.1273
C(16)	0.4637(6)	0.3937(6)	0.2880(6)	0.0768
C(19)	0.4753(7)	0.6402(7)	0.2704(7)	0.0754
C(20)	0.5781(9)	0.7056(7)	0.3667(8)	0.0927
C(21)	0.6151(1)	0.8097(9)	0.4041(1)	0.1230
C(22)	0.5482(2)	0.8521(1)	0.3462(2)	0.1411
C(23)	0.4461(1)	0.7921(1)	0.2542(2)	0.1294
C(24)	0.4098(8)	0.6866(8)	0.2149(9)	0.1064
C(26)	0.2490(6)	0.4087(7)	0.0558(8)	0.0930
C(27)	0.3277(6)	0.3897(6)	0.0206(7)	0.0726
C(29)	0.5165(6)	0.4454(5)	0.0993(6)	0.0625
C(30)	0.4974(6)	0.3764(6)	−0.0032(6)	0.0710
C(31)	0.3917(7)	0.3140(6)	−0.0957(6)	0.0801
C(32)	0.3044(7)	0.3206(6)	−0.0848(7)	0.0837
C(33)	0.6281(6)	0.5161(6)	0.2040(6)	0.0711
C(36)	0.8924(7)	0.5337(8)	0.2158(8)	0.0780
C(37)	0.9968(9)	0.6016(8)	0.2673(9)	0.1192
C(38)	1.058(1)	0.576(2)	0.223(2)	0.1488
C(39)	1.025(2)	0.486(2)	0.132(2)	0.1370
C(40)	0.922(1)	0.418(1)	0.078(1)	0.1299
C(41)	0.8568(7)	0.4425(8)	0.1203(9)	0.0983
C(43)	0.8905(7)	0.7264(6)	0.4350(8)	0.0973
C(44)	0.8930(6)	0.6456(6)	0.4704(8)	0.0779
C(46)	0.8468(5)	0.4674(6)	0.3925(6)	0.0634
C(47)	0.8758(6)	0.4760(6)	0.4962(7)	0.0741
C(48)	0.9185(7)	0.5721(8)	0.5909(7)	0.0855
C(49)	0.9272(7)	0.6583(7)	0.5781(7)	0.0865
C(50)	0.8036(6)	0.3670(6)	0.2874(6)	0.0703
C(53)	0.8001(6)	0.1128(6)	0.2859(7)	0.0711
C(54)	0.8278(7)	0.0280(8)	0.2462(8)	0.1011
C(55)	0.8471(1)	−0.0362(9)	0.2951(1)	0.1309
C(56)	0.8351(1)	−0.0181(1)	0.3831(1)	0.1279
C(57)	0.8085(8)	0.0651(1)	0.4264(9)	0.1159
C(58)	0.7923(6)	0.1297(7)	0.3793(8)	0.0874
C(60)	0.6674(6)	0.1229(5)	0.0241(7)	0.0688

Table 1 (continued)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U_{eq}</i> (Å ²)
C(61)	0.7833(7)	0.1394(6)	0.0600(7)	0.0841
C(63)	0.5768(7)	0.0886(6)	−0.0841(7)	0.0782
C(64)	0.4778(7)	0.0876(6)	−0.0967(6)	0.0789
C(65)	0.4715(6)	0.1156(5)	−0.0018(6)	0.0657
C(66)	0.5624(6)	0.1453(5)	0.1035(6)	0.0600
C(67)	0.5618(6)	0.1751(5)	0.2096(6)	0.0650
S(100) ^a	0.1845(8)	0.8293(7)	0.2368(8)	0.202(3) ^b
S(101) ^a	0.180(1)	0.925(1)	0.301(1)	0.293(6) ^b
O(102)	0.229(1)	0.844(1)	0.340(1)	0.315(7) ^b
C(103)	0.214(1)	0.928(1)	0.218(1)	0.265(8) ^b
C(104)	0.048(2)	0.836(1)	0.212(2)	0.287(8) ^b

^aAtoms have an occupancy of 0.5000.^bAtoms are not refined anisotropically.

Scheme 1. Synthesis of 1.



Scheme 2. Synthesis of 2.

organometallic compounds (see, for example, Refs. [22,23]). In the case of the smaller boron atom only one five-membered chelate is formed, so that the second hydroxy group binds to another boron atom. The preference for the formation of a cyclic structure instead of a polymeric one seems to be highly favored due to the stereochemistry around the boron atoms (Tables 1–4). From Fig. 1 it can be seen that the overall structure is formed by four boronate subunits. The tetrahedral environment of the boron atom and the planarity of the ligand with the collinearity of its primary bonds (Table 3) dictate the tetrameric macrocyclic structure formation. The angles between the four boronate moieties are nearly perpendicular to each other (Table 4). The con-

figuration of the boron atoms is alternate so that S_4 symmetry could be expected for the macrocycle. Actually the point group is only pseudo S_4 due to two effects. The first one is the presence of a solvent molecule (DMSO) in the crystal lattice, which alters the geometry of the nearest boronate unit (around B9); the $N \rightarrow B$ bond length is shorter and the $O-B-N$ bond angle is larger (Table 2). The second one is the distinct torsion of the phenyl groups at the boron atoms (Table 2). The cavity of the structure can be estimated by the distance between two neighboring boron atoms with an average value of 5.42 Å.

Under the conditions described, the reaction is fast and selective. It can be assumed that only the diastere-

Table 2
Selected bond lengths, bond angles and torsion angles for **1**

Bond lengths (Å)			
N(1)–B(9)	1.64(1)	O(42)–B(35)	1.47(1)
N(45)–B(35)	1.68(1)	O(62)–B(52)	1.470(9)
N(28)–B(18)	1.675(9)	O(17)–B(18)	1.429(9)
N(59)–B(52)	1.676(9)	O(34)–B(35)	1.435(9)
O(8)–B(9)	1.455(9)	O(51)–B(52)	1.420(9)
O(25)–B(18)	1.47(1)	O(68)–B(9)	1.447(9)
Bond angles (°)			
B(9)–N(1)–C(2)	109.1(7)	O(8)–C(7)–C(2)	106.5(7)
B(18)–N(28)–C(27)	110.0(6)	O(25)–C(26)–C(27)	107.0(6)
B(35)–N(45)–C(44)	109.2(7)	O(42)–C(43)–C(44)	106.9(7)
B(52)–N(59)–C(60)	109.5(6)	O(62)–C(61)–C(60)	107.1(6)
B(9)–O(8)–C(7)	114.5(7)	O(8)–B(9)–O(68)	113.7(7)
B(18)–O(25)–C(26)	115.6(6)	O(17)–B(18)–O(25)	115.1(7)
B(35)–O(42)–C(43)	114.8(6)	O(34)–B(35)–O(42)	114.5(7)
B(52)–O(62)–C(61)	114.7(6)	O(51)–B(52)–O(62)	114.7(7)
N(1)–B(9)–O(8)	99.3(6)	O(68)–B(9)–C(10)	109.2(7)
N(28)–B(18)–O(25)	97.5(6)	O(17)–B(18)–C(19)	110.4(7)
N(45)–B(35)–O(42)	97.6(6)	O(34)–B(35)–C(36)	109.6(7)
N(59)–B(52)–O(62)	97.5(5)	O(51)–B(52)–C(53)	109.9(7)
N(1)–C(2)–C(7)	110.4(8)	N(1)–B(9)–O(68)	113.7(7)
N(28)–C(27)–C(26)	109.7(7)	N(28)–B(18)–O(25)	108.3(6)
N(45)–C(44)–C(43)	110.4(8)	N(45)–B(35)–O(42)	107.8(6)
N(59)–C(60)–C(61)	110.0(7)	N(59)–B(52)–O(62)	108.9(6)
Torsion angles (°) ^a			
N(1)–B(9)–C(10)–C(11)	128.54		
N(1)–B(9)–C(10)–C(15)	–54.01		
O(8)–B(9)–C(10)–C(11)	–120.27		
O(8)–B(9)–C(10)–C(15)	57.17		
C(24)–C(19)–B(18)–N(28)	77.67		
C(24)–C(19)–B(18)–O(25)	–31.20		
C(20)–C(19)–B(18)–N(28)	–104.73		
C(20)–C(19)–B(18)–O(25)	146.40		
C(37)–C(36)–B(35)–O(42)	31.37		
C(37)–C(36)–B(35)–N(45)	–78.79		
C(41)–C(36)–B(35)–O(42)	–145.91		
C(41)–C(36)–B(35)–N(45)	103.94		
C(54)–C(53)–B(52)–O(62)	–24.38		
C(54)–C(53)–B(52)–N(59)	84.84		
C(58)–C(53)–B(52)–O(62)	151.53		
C(58)–C(53)–B(52)–N(59)	–99.25		

^aA positive rotation is anti-clockwise from atom 1, when viewed from atom 3 to atom 2.

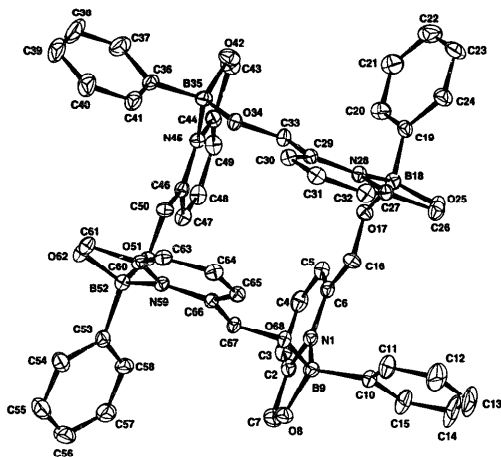


Fig. 1. Crystal structure of 1.

omer observed in the crystal structure analysis (SRSR) is obtained in high yield. Together with the fact that condensation reactions are based on equilibria, a self assembly reaction type can be proposed [24] (for a recent review of this topic, see Ref. [25]). Self-assembly is the spontaneous association of different components to form a complex, highly ordered macromolecular or

supramolecular building that is favored thermodynamically [26].

In a similar manner a dimeric macrocycle has been synthesized. Compound 2 is formed by the condensation of 2-(saicylideneamino)-1-hydroxyethane (H_2 SALAHE) with phenylboronic acid (Scheme 2). This reaction provides the highest yields (71%) in benzene, when a Dean Stark trap is used to separate the water formed during the condensation. Again, the monomer is not formed during this reaction as could be expected in analogy to a series of metal complexes, where H_2 SALAHE acts as a tridentate monochelating ligand (see, for example, Refs. [27,28]). Fig. 2 shows the crystal structure of compound 2 (Tables 5–7), a dimer. The molecule consists of two nearly planar boronate subunits (Table 7). This planarity and the required tetrahedral boron environment are responsible for the preferred dimerization of the compound, with a

Table 3
Deviations from the boronate mean planes in 1^a

Atom	$\Delta(\text{\AA})$	Atom	$\Delta(\text{\AA})$	Atom	$\Delta(\text{\AA})$	Atom	$\Delta(\text{\AA})$
Plane 1 ^b		Plane 2 ^c		Plane 3 ^d		Plane 4 ^e	
N(1)	0.000	N(28)	-0.004	N(45)	0.003	N(59)	0.005
C(2)	0.014	C(29)	0.009	C(46)	0.012	C(63)	0.022
C(3)	-0.017	C(30)	-0.005	C(47)	-0.017	C(64)	-0.009
C(4)	0.007	C(31)	-0.003	C(48)	0.007	C(65)	-0.006
C(5)	0.007	C(32)	0.307	C(49)	0.007	C(66)	0.008
C(6)	-0.011	C(27)	-0.005	C(44)	-0.013	C(60)	-0.020
Deviations from the mean planes ($\text{\AA}$)							
C(7)	0.057	C(26)	-0.050	C(43)	-0.070	C(61)	-0.117
O(8)	0.133	O(25)	-0.143	O(42)	-0.245	O(62)	-0.295
B(9)	0.020	B(18)	-0.089	B(35)	-0.062	B(52)	-0.088

^aPlane 1, $14.45091X - 1.52010Y - 9.34943Z = 3.463$, plane 2, $-0.20754X + 14.26988Y - 9.42824Z = 5.304$, plane 3, $14.38461X - 2.06331Y - 4.13601Z = 9.851$, plane 4, $-0.09938X - 14.60381Y + 4.33318Z = -1.737$. X, Y, Z are orthogonal coordinates w.r.t. axes a, b, c ; Δ is the deviation from planes.

^bPlane 1 is calculated between N(1), C(2) until C(6).

^cPlane 2 is calculated between N(28), C(27), C(29) until C(32).

^dPlane 3 is calculated between N(45), C(44), C(46) until C(49).

^ePlane 4 is calculated between N(59), C(60), C(63) until C(66).

Table 4
Dihedral angles between the boronate mean planes in 1

Planes ^a	Dihedral angle ($^\circ$) ^b
1 and 2	87.15
2 and 3	96.08
3 and 4	90.92
4 and 1	88.64

^aPlanes are described in Table 3.

^bThe dihedral angle between the normals to the planes.

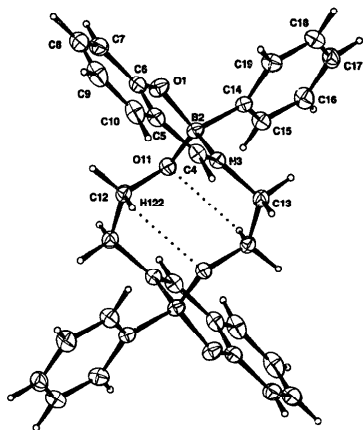


Fig. 2. Crystal structure of 2.

tridentate chelation around the boron atom being too strained. The macrocyclic structure is based on a ten-membered heterocyclic ring in a boat-chair-boat conformation. The molecule is symmetric with an inversion center and belongs to the C_i point group. Interestingly, the distance of 2.43 Å between one of the hydrogen atoms of the OCH_2 group and the opposite oxygen atom is below the sum of the van der Waals radii (the sum of the van der Waals radii of oxygen and hydrogen

Table 5
Atomic coordinates and isotropic thermal parameters for 2

Atom	x/a	y/b	z/c	$U_{\text{eq}}(\text{\AA}^2)$
O(1)	-0.1195(2)	-0.0688(2)	0.1414(2)	0.0473
O(11)	0.0447(2)	0.1036(2)	0.4041(2)	0.0410
B(2)	-0.1358(4)	0.0058(3)	0.2926(3)	0.0391
N(3)	-0.2535(3)	-0.1594(2)	0.3150(2)	0.0386
C(4)	-0.2864(3)	-0.3187(3)	0.2258(3)	0.0456
C(5)	-0.2321(3)	-0.3644(3)	0.0957(3)	0.0441
C(6)	-0.1473(3)	-0.2340(3)	0.0579(2)	0.0430
C(7)	-0.0968(4)	-0.2772(4)	-0.0702(3)	0.0539
C(8)	-0.1359(5)	-0.4515(5)	-0.1590(3)	0.0599
C(9)	-0.2214(5)	-0.5809(4)	-0.1242(4)	0.0593
C(10)	-0.2685(4)	-0.5401(3)	0.0023(3)	0.0557
C(12)	0.1660(4)	0.0192(3)	0.4104(3)	0.0425
C(13)	-0.3223(4)	-0.1278(3)	0.4434(3)	0.0453
C(14)	-0.2541(3)	0.1218(3)	0.3020(2)	0.0387
C(15)	-0.1978(4)	0.2886(3)	0.4173(3)	0.0482
C(16)	-0.3060(4)	0.3836(3)	0.4233(3)	0.0545
C(17)	-0.4734(4)	0.3153(4)	0.3173(3)	0.0530
C(18)	-0.5339(4)	0.1511(4)	0.2007(3)	0.0567
C(19)	-0.4242(4)	0.0585(3)	0.1952(3)	0.0502

Table 6
Selected bond lengths, bond angles and torsion angles for 2

Bond lengths (Å)			
O(1)–B(2)	1.492(3)	O(11)–B(2)	1.453(3)
B(2)–N(3)	1.624(3)	B(2)–C(14)	1.601(3)
N(3)–C(4)	1.291(3)	C(4)–C(5)	1.427(3)
O(1)–C(6)	1.332(3)	O(11)–C(12)	1.412(3)
N(3)–C(13)	1.477(3)		
Bond angles (°)			
B(2)–O(1)–C(6)	126.5(2)	B(2)–O(11)–C(12)	118.7(2)
O(1)–B(2)–O(11)	111.6(2)	O(1)–B(2)–N(3)	106.5(2)
O(11)–B(2)–N(3)	109.0(2)	O(11)–B(2)–C(14)	109.4(2)
O(11)–B(2)–C(14)	111.9(2)	N(3)–B(2)–C(14)	108.1(2)
B(2)–N(3)–C(4)	122.4(2)	B(2)–N(3)–C(13)	119.4(2)
C(4)–N(3)–C(13)	118.2(2)	N(3)–C(4)–C(5)	122.8(2)
C(4)–C(5)–C(6)	119.4(2)	O(1)–C(6)–C(5)	120.4(2)
O(11)–C(12)–C(13)	109.6(2)	N(3)–C(13)–C(12)	113.0(2)
B(2)–C(14)–C(15)	123.1(2)	B(2)–C(14)–C(19)	121.3(2)
Torsion angles (°) ^a			
B(2)–N(3)–C(13)–C(12)	62.23		
B(2)–N(3)–C(4)–C(5)	– 3.74		
B(2)–O(1)–C(6)–C(5)	12.68		
B(2)–O(11)–C(12)–C(13)	– 165.18		
N(3)–B(2)–O(1)–C(6)	– 17.09		
N(3)–B(2)–O(11)–C(12)	60.44		
N(3)–C(13)–C(12)–O(11)	– 58.14		
N(3)–C(4)–C(5)–C(6)	3.69		
O(1)–B(2)–N(3)–C(4)	12.38		
O(11)–B(2)–N(3)–C(13)	– 169.09		
O(11)–B(2)–O(11)–C(12)	– 56.99		
O(1)–C(6)–C(5)–C(4)	– 0.83		
C(4)–N(3)–B(2)–C(14)	129.88		
C(4)–N(3)–B(2)–O(11)	– 108.24		
C(4)–N(3)–C(13)–C(12)	116.36		
C(5)–C(4)–N(3)–C(13)	177.72		
C(6)–O(1)–B(2)–C(14)	– 133.72		
C(6)–O(1)–B(2)–O(11)	101.82		
C(14)–B(2)–O(11)–C(12)	179.98		
C(14)–B(2)–N(3)–C(13)	– 51.60		
O(11)–B(2)–N(3)–C(13)	70.29		

^aA positive rotation is anti-clockwise from atom 1, when viewed from atom 3 to atom 2.

Table 7
Deviations from the boronate mean plane in 2^a

Atom	$\Delta(\text{\AA})$
Plane 1 ^b	
C(5)	-0.002
C(6)	0.008
C(7)	-0.005
C(8)	-0.002
C(9)	0.008
C(10)	-0.005
Deviations from the mean plane (Å)	
C(4)	0.037
N(3)	0.024
O(1)	0.070
B(2)	-0.129

^aPlane 1, $-6.77010X + 3.39794Y - 3.71838Z = -0.020$; X, Y, Z are orthogonal coordinates w.r.t. axes a, b, c; Δ is the deviation from the plane.

^bPlane 1 is calculated between C(5) until C(10).

is 2.70 Å [29]) indicating a transannular interaction (Fig. 2).

3. Conclusions

The above discussion has shown that macrocyclic oligoboronates can easily be formed, when aminodialcohol ligands of appropriate geometry are present. A key point is the formation of a dative $N \rightarrow B$ bond providing rigidity to the structure.

As already mentioned in the introduction, the present macrocyclic compounds could serve as receptors for Lewis bases and even anionic molecules, if the dative $N \rightarrow B$ bond is broken, so that the Lewis acidity of the boron atom can be exploited. In the case of an application as anionic host the nitrogen atom could be transformed to an ammonium ion, so that the overall host-guest molecule would be neutral.

Up to now the host-guest chemistry of compounds **1** and **2** has not been carried out due to their insolubility. Therefore the introduction of functional groups into the ligands is underway in order to undertake further studies.

4. Experimental

All reagents were used as received from commercial suppliers. $H_2SALAHE$ (2-(salicylideneamino)-1-hydroxyethane) was prepared by refluxing equimolar quantities of ethanolamine and salicylaldehyde in benzene for 30 min. The solvent and the water formed during the reaction were removed by a Dean Stark trap to yield a yellow oil that was used without further purification.

Elemental microanalyses were performed by Oneida Research Services, Whitesboro, NY 13492.

Data for the X-ray crystal structure determination of **1** and **2** were collected by an Enraf Nonius CAD4 diffractometer. $\lambda(\text{MoK}\alpha) = 0.71069$ Å, monochromator: graphite, $T = 293$ K, ω - 2θ scan, range $2^\circ < \theta < 26^\circ$.

4.1. Preparation of 4,14,24,34-tetraphenyl-[3,5,13,15,23,25,33,35]octaoxa[41,42,43,44]tetraaza[4,14,24,34]-tetraborapentacyclo[31.3.1.1^{7,11}.1^{17,21}.1^{27,31}]dodecatetraene-1 (41), 7,9,11(42),17,19,21(43),27,29,31(44),37,39-dodecaene(1)

A solution of phenylboronic acid (0.44 mg, 3.60 mmol) in ethyl acetate was added to a solution of 2,6-pyridinedimethanol (0.50 mg, 3.60 mmol) in ethyl acetate. The combined solutions were stirred and after a few seconds a white precipitate formed. The solid was

collected by filtration, washed with small amounts of ethyl acetate and dried. The product is insoluble in all common solvents. Yield: 93%. M.p. 278°C (dec.); IR (KBr) $\tilde{\nu}(\text{cm}^{-1})$: 3068 (C–H_{arom}), 2928 (C–H_{aliph}), 1654, 1646 (C=N), 1636, 1622 (C=N, C=C), 1252, 1196, 1090 (B–C, B–O, C–O), 826, 790, 746, 704, 668 (C–H_{arom}).

Elemental analysis: calc.: C, 69.38, H, 5.37, N, 6.22%. found: C, 68.01, H, 5.26, N, 5.81%.

4.2. X-ray crystallography of **1**

A small amount of compound **1** was heated in DMSO and cooled slowly, whereupon suitable crystals for X-ray diffraction were formed.

Crystal data: Colorless cubic crystals of compound **1**, $C_{55}H_{49}B_4N_4O_8 \cdot DMSO$ ($M = 978.34$ g mol⁻¹), crystallize in the triclinic spacegroup $P\bar{1}$ (no. 2), crystal dimensions $0.25 \times 0.25 \times 0.30$ mm³, $a = 14.757(1)$, $b = 14.949(1)$, $c = 15.112(1)$ Å, $\alpha = 112.03(1)^\circ$, $\beta = 117.998(5)^\circ$, $\gamma = 96.325(5)^\circ$, $V = 2556.4(3)$ Å³ by least squares refinement on diffractometer angles for 24 automatically centered reflections, $Z = 2$, $\rho_{\text{calc}} = 1.35$ Mg m⁻³, $\mu = 0.09$ mm⁻¹. A total of 10427 reflections was measured, of which 10013 were independent and of these 3134 were considered observed [$F > 3\sigma(F)$], absorption correction was not necessary ($C_{\text{min}/\text{max}} = 0.963/0.969$), corrections were made for Lorentz and polarization effects. Solution and refinement: direct methods (SHELXS-86) for structure solution. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were calculated and refined with an overall isotropic thermal parameter. The disordered DMSO molecule was only refined isotropically (CRYSTALS, version 9, 1994). $R = 0.060$, $R_w = 0.053$ from 3134 reflections with $F > 3\sigma(F)$ for 635 variables against $|F|$, $w = 1/\sigma^2(F)$, $s = 3.04$. Largest residual electron density peak/hole in the final difference map: $\rho_{\text{max}} = 0.43$, $\rho_{\text{min}} = -0.36$ e/Å³, max Δ/σ shift 0.098.

4.3. Preparation of 2,11-diphenyldibenzol[h,q][7,16]diiiminol[1,3,10,12]traoxa[2,11]diboracyclooctadecane (2)

A solution of phenylboronic acid (0.37 mg, 3.00 mmol) in benzene was added to a solution of 2-(salicylideneamino)-1-hydroxyethane ($H_2SALAHE$) (0.50 mg, 3.00 mmol) in 5 ml of benzene. The combined solutions were heated to reflux. After 15 min a yellow precipitate formed. The reaction was completed by water separation with a Dean Stark trap. The solid was collected by filtration, washed with a small amount of benzene and dried. The yellow product is insoluble in all common solvents. Yield: 71%. M.p. $> 300^\circ\text{C}$ (dec.); IR (KBr) $\tilde{\nu}(\text{cm}^{-1})$: 3044 (C–H_{arom}), 2964, 2932 (C–

H_{aliph.}), 1640 (C = N), 1560 (C = N, C = C), 1314 (C–O_{phenoxyl}), 1200, 1138, 1124, 1110 (B–O, B–C, C–O_{alcoh.}), 756, 748, 740, 712, 652 (C–H_{arom.})

Elemental analysis: calc.: C, 71.75, H, 5.62, N, 5.58% found: C, 69.08, H, 5.42, N, 5.45%.

4.4. X-ray crystallography of 2

Crystals suitable for X-ray diffraction were obtained, when the reaction was performed in a small amount of dichloromethane at room temperature without stirring.

Crystal data: Yellow cubic crystals of compound 2, C₃₀H₂₈B₂N₂O₄ (*M* = 502.18 g mol⁻¹), crystallize in the triclinic spacegroup P1̄ (no. 2), crystal dimensions 0.2 × 0.4 × 0.4 mm³, *a* = 7.9161(4), *b* = 9.0827(8), *c* = 10.3632(5) Å, *α* = 112.828(7), *β* = 99.082(5), *γ* = 108.194(6)°, *V* = 618.42(8) Å³ by least squares refinement on diffractometer angles for 24 automatically centered reflections, *Z* = 1 (the molecule is located at an inversion center), *ρ*_{calc'd} = 1.40 Mg m⁻³, *μ* = 0.09 mm⁻¹. A total of 3160 reflections was measured, of which 2976 were independent and of these 1639 were considered observed [*F* > 3σ(*F*)], absorption correction was not necessary (*C*_{min/max} = 0.966/0.983), corrections were made for Lorentz and polarization effects. Solution and refinement: direct methods (SHELXS-86) for structure solution. Non hydrogen atoms were refined anisotropically. Hydrogen atoms were located from the difference Fourier map and refined with an overall isotropic thermal parameter (CRYSTALS, version 9, 1994). *R* = 0.040, *R*_w = 0.035 from 1639 reflections with *F* > 3σ(*F*) for 216 variables against |*F*|, *w* = 1/σ²(*F*), *s* = 2.87. Largest residual electron density peak/hole in the final difference map: *ρ*_{max} = 0.20, *ρ*_{min} = -0.14 e/Å³, max Δ/σ shift 0.01.

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