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New boron macrocycles based on self-assembly of Schiff bases

Victor Barba, Edmundo Gallegos, Rosa Santillan, Norberto Farfán *

Depto. de Química, Centro de Investigación y de Estudios Avanzados del IPN, Apdo. Postal 14-740, 07000 México D.F., Mexico

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Abstract

In order to investigate the formation of macrocyclic boronates, we carried out the reaction of 3-aminophenyl boronic acid with salicylaldehyde, 2-hydroxyacetophenone and 2-hydroxybenzophenone. In all cases, macrocyclic structures were formed and the X-ray crystallographic study of the trimeric complex derived from 2-hydroxyacetophenone showed that the macrocyclic system is asymmetric.

Keywords: Schiff bases; Imines; Macrocyclic boronates; Self-assembly

1. Introduction

Macrocyclic structures containing Schiff bases have been obtained by different methods [1–6]. The development of these methods cleared the way to the design and synthesis of new ligands that offered a series of coordinating sites. Thus several dicarbonyl precursors and a wide range of diamines have been used [7–11] whereby, the [1 + 1], [2 + 2] and [2 + 3] condensation products led to the formation of new macrocycles by self-assembly processes. Self-assembly processes allow the construction of highly ordered molecular or supramolecular molecules directly and spontaneously [12]. The presence of metal ions with the appropriate ionic radius has also allowed the synthesis of coordinating systems via the template effect [13–16].

We are interested in the synthesis of boron macrocyclic systems [17–22] derived from tridentate ligands having one nitrogen and two oxygen donor atoms, as shown in Scheme 1. In these systems one of the oxygen atoms forms a five- or six-membered ring while the other one is involved in the formation of an intermolecular boron–oxygen bond. The nitrogen atom almost always forms a coordinative bond with the boron atom [22].

We have reported previously the synthesis of dimeric boronates [17–21] derived from Schiff bases and arylboronic acids, as well as a tetrameric boronate obtained by self-assembly of 2,6-pyridinedimethanol and phenylboronic acid [17]. In all cases the boron atom has a distorted tetrahedral geometry and the compounds present transannular interactions between the nitrogen and boron atoms with distances between 1.601 (9) and 1.667 (9) Å, that are characteristic for dative N–B bonds [17–28]. Herein, we describe the preparation and structural characterization of new macrocyclic boronates obtained by condensation of *o*-hydroxybenzenecarbonyl systems with 3-aminophenylboronic acid.

2. Results and discussion

The preparation of compounds **1**, **2** and **3** was developed based on the strategy previously described for the formation of macrocyclic boron compounds to design new systems. The coupling reaction of 2-hydroxyacetophenone, 2-hydroxybenzophenone and salicylaldehyde with 3-aminophenylboronic acid in a 1:1 molar ratio under reflux of methanol provided yellow precipitates corresponding to compounds **1**, **2** and **3**, in moderate yields (Scheme 2).

The formation of macrocyclic systems **1**, **2** and **3** was carried out by condensation of *o*-hydroxybenzenecarbonyl compounds with 3-aminophenylboronic acid as shown in Scheme 3. The first step involves formation of

* Corresponding author. Tel.: +52-5-7473721; fax: +52-5-7477113.

E-mail address: jfarfan@mail.cinvestav.mx (N. Farfán).

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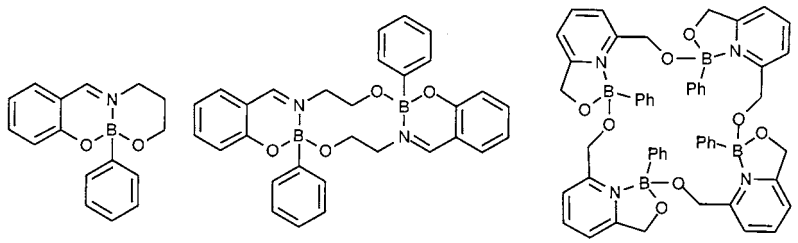


Scheme 1. Monomeric, dimeric and tetrameric structures obtained from tridentate ligands and phenylboronic acid.

imine I followed by condensation of several units to give trimeric or tetrameric structures II. In the last step, the hydroxyl groups present in the macrocycle are substituted by MeO thus avoiding, a possible polymerization.

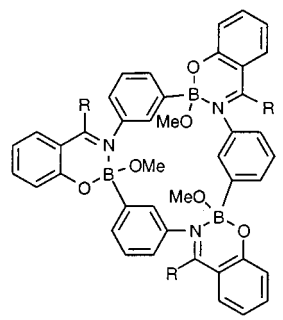
Elemental microanalyses and techniques spectroscopic allowed to fully characterize the new macrocycles **1**, **2** and **3**. The IR spectra exhibited a strong adsorption band at 1610, 1608 and 1626 cm^{-1} for **1**, **2** and **3**, respectively, assigned to the ν(C=N) band. The highest wavenumber corresponds to the tetrameric compound and it is in accordance with similar systems. For compounds **1** and **2,** the adsorption band is shifted to lower wavenumbers due to the effect of the methyl and phenyl groups on the stretching band corresponding to the C=N bond.

Mass spectral analysis of **1** and **2** allowed to establish their trimeric structures, while the data shown by the FAB spectrum of the salicylaldehyde derivative (**3**), corresponded to a tetrameric structure. The differences in ring size are due to steric hindrance between the substituent at the imine group and the aromatic moiety of the boronic acid. Therefore, the steric effect of the methyl and phenyl groups with a proton of the nearby aromatic ring has an important influence on the formation of trimeric structures. This effect is not present in compound **3**, which has one hydrogen atom at the imine group. As seen from the NMR spectra and the X-ray structure (vide infra), the boron bound hydroxyl group undergoes substitution by MeO group through an alcoholysis reaction.

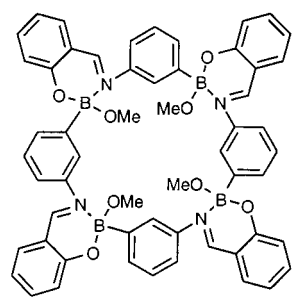
Compounds **2** and **3** were insoluble in all common solvents so that its characterization by NMR was not possible, however, compound **1** was slightly soluble in CH_2Cl_2 and it was characterized by NMR spectroscopy. It should be noted that both the ^{13}C- and ^{1}H-NMR spectra were strongly indicative of the asymmetric nature of the compound. For instance the ^{13}C-NMR spectrum showed three signals at 172.8, 172.2 and 171.8 ppm assigned to the C=N carbon; due to this asymmetry, assignment of the signals in the aromatic region was not possible and only sets of three signals are given. The ^{1}H-NMR spectrum was also complex and the only distinguishable signal was that of the methyl groups at low field. A broad signal was observed in ^{11}B-NMR at 7.0 ppm which confirmed the tetrahedral character for the boron atoms [29].

The structure of complex **1** was confirmed by single crystal X-ray diffraction analysis showing that it consists of three asymmetrically oriented [B_3(OMe)-μ-$(SAP)_3$] [30] units with a core ring of 15 members. Initially we thought that it was possible to prepare a molecule with a C_3 symmetry since we have found in previous studies dimeric [17] and tetrameric [17] structures having C_i and pseudo S_4 symmetry, however, as seen in Fig. 1, that is not the case here. The lack of symmetry can be attributed to high annular tension at the aromatic links.

In each case the boron atoms are chelated by the ligand (SAP) and one alkoxide fragment, resulting in a



1: R = Me, **2**: R = Ph



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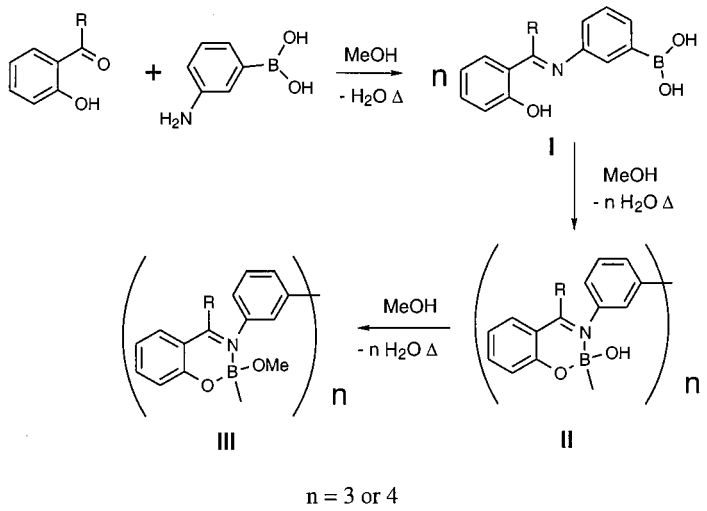
Scheme 2. Macrocyclic boronates obtained by condensation of 3-aminophenylboronic acid with 2-hydroxyacetophenone (**1**), 2-hydroxybenzophenone (**2**) and salicylaldehyde (**3**).



Scheme 3. Mechanistic pathway for the formation of macrocyclic systems.

distorted T_d geometry. The angles around the boron atom are close to tetrahedral having values from 102.1 (3) to 116.1(3)°. The N–B bond lengths are normal for tetrahedral boron complexes obtained from salicylidene derivatives and they are in accordance with a donor-acceptor character [23]. The N–B distance of 1.632 (5) Å (average) is indicative of a strong coordinating ability of the nitrogen on the boron atom.

The two B–O bond lengths differ significantly due to the fact that one is in a cyclic system while the other one is acyclic. The B–O(Ar) distance (average 1.482(5) Å) is slightly longer than the B–OMe bond (average 1.413(5) Å) and both are in accordance with similar complexes derived from Salen $(B(OR)_2)_2$ ligands [31,32]. The chelating imine ligands offer no unusual bonding features, bond lengths and angles in the C=N–C units are comparable to those in other structurally characterized complexes with this group. Typical molecular features are the large O–B–O and small O–B–N angles, as observed in many other complexes derived from tridentate Schiff base ligands [17–21].

In the crystal, the trinuclear complexes for **1** are stacked along the crystallographic x axis producing long channels (Fig. 2) through hydrogen bonding interactions of 2.402 Å that produce extented structures.

3. Conclusions

The present study has demonstrated that supramolecular systems can be exploited by combining a boronic acid and strategically designed reagents to create new macrocyclic compounds. Logical extensions of this strategy which allow the synthesis of more complex self-assembled systems are currently under investigation in our laboratory.

4. Experimental

4.1. Reagents and instrumentation

All starting materials were obtained commercially from Aldrich Chemical Company. Solvents were used without further purification, but single crystals were grown from spectrophotometric grade solvent.

NMR spectra were recorded on Bruker Avance DPX 300 spectrometer. Chemical shifts (ppm) are relative to $(CH_3)_4Si$ (^1H and ^{13}C) and BF_3OEt_2(^{11}B). Infrared spectra were recorded on a Perkin Elmer 16F-PC FT-IR spectrophotometer. Mass spectra were obtained with a HP 5989 A spectrometer. Melting points were obtained

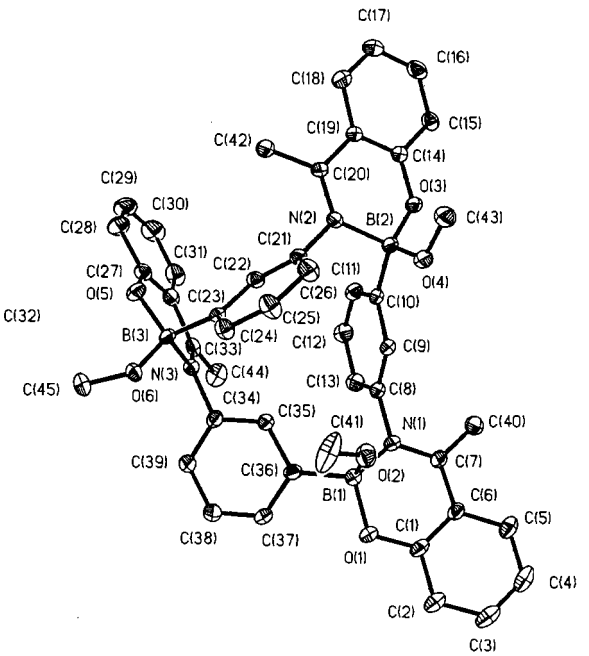


Fig. 1. ORTEP diagram of the molecular structure of compound **1**.

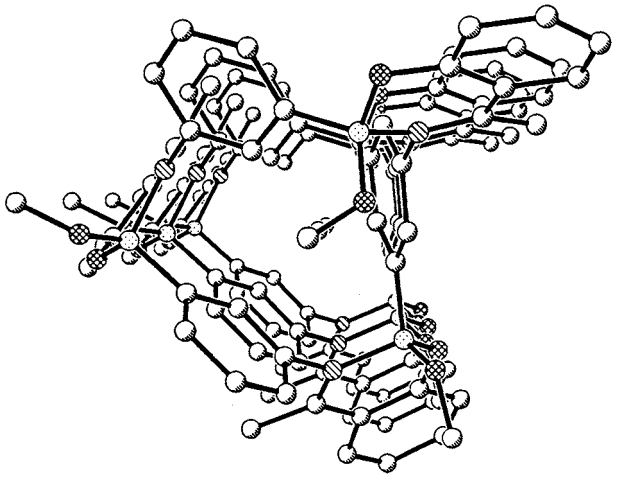


Fig. 2. Packing of trinuclear complex **1** along the x-axis.

Table 1
Crystal data of compound **1**

Empirical formula	$C_{45}H_{42}B_3N_3O_6$
Crystal dimensions (mm)	$0.52 \times 0.26 \times 0.16$
Molecular weight (g mol^{-1})	753.25
Space group	P-1
a (Å)	9.289 (2)
b (Å)	12.305 (2)
c (Å)	18.540 (4)
α (°)	104.71 (3)
β (°)	95.10 (3)
γ (°)	105.76 (3)
V (Å^3)	1944.1 (7)
μ (mm^{-1})	0.084
D_{calc} (g cm^{-3})	1.287
Z	2
θ range for data collection (°)	4.60–52.22
Temperature (°)	243 K
Reflections collected/unique	8000/7504
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7502/0/515
Goodness-of-fit on F^2	0.974
Final R Indices [$F>4\sigma(F)$]	$R_1 = 0.0502$, $wR_2 = 0.1403$
R indices (all data)	$R_1 = 0.2088$, $wR_2 = 0.2110$

on a Gallenkamp MFB-595 apparatus and are uncorrected. Elemental microanalyses were performed by Oneida Research Services (Whitesboro, NY 13492).

4.2. General method for the preparation of compounds *1–3*

An equimolecular amount of salicylaldehyde, 2-hydroxyacetophenone or 2-hydroxybezophenone was added to a solution of 3-aminophenylboronic acid in methanol (usually about 10 ml for 2–3 mmol). The mixture was refluxed for 4 h and quantified by water and solvent separation with a Dean Stark trap. The solid obtained was collected by filtration under vacuum and washed with small amounts of methanol and acetone.

4.2.1. Preparation of trimethoxy-[tris-[μ-(3-phenyl-κC) imino-κN] ethylphenolato-(2-)-κO] triboron (*1*)

Compound **1** was prepared from 0.5 g (3.67 mmol) of 2-hydroxyacetophenone and 0.57 g (3.67 mmol) of 3-aminophenylboronic acid monohydrate, a yellow solid was obtained (Yield: 0.44 g, 0.58 mmol, 48%), crystals suitable for X-ray diffraction were obtained from methanol after standing for 3 days without stirring. m.p. = 329°C, IR $\bar{\nu}$(KBr) 2936, 2818, 1610 (C=N), 1552, 1346, 1274, 1230, 1154, 1106, 972, 752 cm^{-1}; MS m/z (%): 721 (M^+–OCH_3, 1), 689 (15), 656 (8), 504 (31), 503 (100), 471 (76), 395 (5), 379 (2), 252 (53), 238 (2), 162 (2); ^{1}H-NMR (300 MHz, CD_2Cl_2) δ: 7.80–6.00 (24H, m, H–Ar), 2.32, 2.30, 2.29 (3H each, s, OMe), 2.24, 2.18, 2.17 (3H each, s, Me) ppm; ^{13}C-NMR (75 MHz, CD_2Cl_2) δ: 172.8, 172.2 and 171.8 (C=N), 160.8, 166.7 and 160.3 (C_{Ar}–O), 141.6, 140.2, 137.2, 136.9, 133.0, 132.2, 131.3, 131.0, 130.9, 129.5, 128.5, 128.1, 127.7, 127.0, 126.8, 123.6, 123.2, 122.8, 120.5, 120.1, 120.0, 119.5, 119.05, 119.0, 118.5, 118.1, 117.5, 116.9 (C–Ar), 50.4, 49.8 and 49.0 (OMe), 19.5, 18.7 and 18.3 (Me) ppm; ^{11}B-NMR (96 MHz, CD_2Cl_2) δ: +7.0 ppm ($h_{1/2}$ = 674.03 Hz). Anal. Found: C, 71.87; H, 5.15; N, 5.65. Calc. for $C_{45}H_{42}B_3N_3O_6$: C, 71.71; H, 5.58; N, 5.58%.

4.2.2. Preparation of trimethoxy-[tris-[μ-(3-phenyl-κC) imino-κN] benzylphenolato-(2-)-κO] triboron (*2*)

Compound **2** was prepared from 0.5 g (2.52 mmol) of 2-hydroxybenzophenone and 0.35 g (2.52 mmol) of 3-aminophenylboronic acid monohydrate, a yellow solid was obtained (Yield: 0.52 g, 0.55 mmol, 65%), that was insoluble in all common solvents. m.p. = 329–331°C. IR $\bar{\nu}$(KBr) 2920, 2850, 1608 (C=N), 1588, 1542, 1472, 1152, 976, 756 cm^{-1}; MS m/z (%): 909 (M^+–OCH_3, 1), 627 (10), 597 (5), 315 (15), 314 (100), 250 (46), 238 (38), 237 (10), 103 (2), 78 (1). Anal. Found: C, 76.91; H, 5.09; N, 4.47. Calc. for $C_{60}H_{48}B_3N_3O_6$: C, 76.72; H, 5.11; N, 4.48%.

4.2.3. Preparation of tetramethoxy-[tetrakis-[μ-(3-phenyl-κC) imino-κN] methylphenolato-(2-)-κO] tetraboron (*3*)

Compound **3** was prepared from 0.5 g (4.09 mmol) of salicylaldehyde and 0.63 g (4.09 mmol) of 3-aminophenylboronic acid monohydrate. A yellow solid was obtained (Yield: 0.62 g, 0.66 mmol, 64%), that was insoluble in all common solvents. m.p. = 349–351°C, IR $\bar{\nu}$(KBr) 3414, 2922, 2850, 1626 (C=N), 1578, 1458, 1312, 1226, 1148, 1096, 750 cm^{-1}, FAB, m/z: 948, 921, 889, 859, 843, 817, 804, 788, 766, 749, 722, 719, 687, 677, 651, 635, 613, 612, 587, 550, 549, 522, 511. Anal. Found: C, 70.54; H, 5.07; N, 5.61. Calc. for $C_{56}H_{48}B_4N_4O_8$: C, 70.88; H, 5.06; N, 5.90%.

Table 2
Selected bond distances (Å), bond angles (°) and torsion angles (°) for **1**

Bond distances					
N(1)–B(1)	1.632(6)	N(2)–B(2)	1.626(5)	N(3)–B(3)	1.639(5)
O(1)–B(1)	1.483(5)	O(3)–B(2)	1.487(5)	O(5)–B(3)	1.477(5)
O(2)–B(1)	1.417(6)	O(4)–B(2)	1.409(5)	O(6)–B(3)	1.414(5)
N(1)–C(7)	1.301(5)	N(2)–C(20)	1.311(4)	N(3)–C(33)	1.298(5)
N(1)–C(8)	1.446(5)	N(2)–C(21)	1.445(4)	N(3)–C(34)	1.448(4)
C(36)–B(1)	1.608(6)	C(10)–B(2)	1.612(6)	C(23)–B(3)	1.594(6)
O(1)–C(1)	1.340(4)	O(3)–C(14)	1.336(4)	O(5)–C(27)	1.326(5)
Bond angles					
O(2)–B(1)–N(1)	102.1(3)	O(4)–B(2)–N(2)	109.5(3)	O(6)–B(3)–N(3)	110.7(3)
O(1)–B(1)–N(1)	105.6(3)	O(3)–B(2)–N(2)	106.8(3)	O(5)–B(3)–N(3)	105.8(3)
C(36)–B(1)–N(1)	112.8(3)	C(10)–B(2)–N(2)	107.7(3)	C(23)–B(3)–N(3)	108.0(3)
O(2)–B(1)–O(1)	112.9(4)	O(4)–B(2)–O(3)	112.8(3)	O(6)–B(3)–O(5)	109.9(3)
O(1)–B(1)–C(36)	106.8(3)	O(3)–B(2)–C(10)	109.9(3)	O(5)–B(3)–C(23)	111.5(3)
O(2)–B(1)–C(36)	116.1(3)	O(4)–B(2)–C(10)	110.0(3)	O(6)–B(3)–C(23)	110.8(3)
Torsion angles					
C(8)–N(1)–B(1)–C(36)	44.92	C(21)–N(2)–B(2)–C(10)	52.96	C(34)–N(3)–B(3)–C(23)	72.76
C(8)–N(1)–B(1)–O(2)	−80.42	C(21)–N(2)–B(2)–O(4)	−66.61	C(34)–N(3)–B(3)–O(6)	−48.76
C(8)–N(1)–B(1)–O(1)	161.28	C(21)–N(2)–B(2)–O(3)	170.92	C(34)–N(3)–B(3)–O(5)	−167.78
C(7)–N(1)–B(1)–O(1)	−31.89	C(20)–N(2)–B(2)–O(3)	−8.40	C(33)–N(3)–B(3)–O(5)	17.11
C(7)–N(1)–B(1)–O(2)	86.41	C(20)–N(2)–B(2)–O(4)	114.07	C(33)–N(3)–B(3)–O(6)	136.13
C(7)–N(1)–B(1)–C(36)	−148.25	C(20)–N(2)–B(2)–C(10)	−126.36	C(33)–N(3)–B(3)–C(23)	−102.35

4.3. X-ray structure determination

Crystal data, data collection and refinement parameters are listed in Table 1, selected bond distances, bond angles and torsion angles are summarized in Table 2. X-ray measurements were performed with an Enraf–Nonius CAD4 difractometer using graphite monocromator Mo–K_α radiation. The structure was solved by direct methods using the SHELXS-86 [33] program and refinement on F^2 using all data by full-matrix least-square procedures with SHELXS-93 [34]. All non-hydrogen atoms were refined with anisotropic temperature parameters. Hydrogen atoms were determined by difference Fourier maps and their positions as well as one overall isotropic thermal parameter were refined. $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 149207. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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