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Synthesis and molecular structure of a novel barium arylspiroboronate ester

Invited Paper

Nathan R. Halcovitch[1], Michael J. Geier[1], Christopher M. Vogels[1],
Andreas Decken[2†], Stephen A. Westcott[1*]

[1]Department of Chemistry, Mount Allison University
Sackville, NB E4L 1G8, Canada

[2]Department of Chemistry, University of New Brunswick
Fredericton, NB E3B 5A3, Canada

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Abstract: The compound barium bis{bis-(4,6-di-tert-butyl[1,2-benzenediolato(2-)-O,O']borate)} has been prepared by the addition of 3,5-di-tert-butylcatechol to a solution of boric acid and $Ba(OH)_2$ and characterized by a single crystal X-ray diffraction study. The title compound crystallized in the triclinic space group P-1, with cell parameters a = 13.280(2) Å, b = 15.755(3) Å, and c = 16.980(3) Å, α = 71.691(2)o, β = 79.528(3)o, γ = 80.741(3)o, Z = 1, and V = 3296.1(10) Å^3. The structure was solved by direct methods and refined to a final R = 0.0459 for 14370 reflections with $I > 2\sigma(I)$. One of the arylspiroboronate ester counterions is bound to the barium atom in a rare example of the η1 bonding mode via a single oxygen of one of the catecholato groups. The coordination sphere around the barium is complemented by four molecules of water, one molecule of acetone and two bridging water molecules, connecting to an adjacent barium atom.

Keywords: *Arylspiroboronate Esters •Barium • Catechol • Coordination*

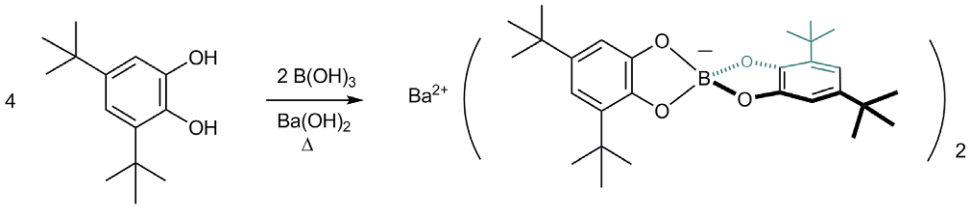
1. Introduction

Arylspiroboronate esters are a remarkable class of compounds containing two catecholato groups bound to a central boron atom. These compounds are usually nontoxic, inexpensive and thermally, chemically and electrochemically stable and have found widespread applications in chemistry and industry. For instance, lithium salts of arylspiroboronate esters are being considered for their potential use as electrolytes in batteries [1]. These compounds have also been used as catalysts, or co-catalysts, for the Diels-Alder reaction [2], methoxycarbonylation reactions [3], and in amide and ester condensation reactions [4].

Of particular interest to us is the ability of these species to bind to metals using different coordination sites. For instance, a nickel complex containing the parent $[Bcat_2]^-$ (cat = 1,2-$O_2C_6H_4$) anion is believed to coordinate to the metal using the Lewis basic oxygen atoms (Fig. 1a) [5]. A similar bonding motif has been reported for a titanium compound (Fig. 1b), isolated as a deactivated form of a catalyst used in the hydroboration of alkenes [6]. Interestingly, rhodium complexes containing these ligands can have the metal fragment bound to the six-membered ring of one of the catecholato groups (Fig. 1c). These rhodium complexes are active and selective catalysts for the hydroboration of a wide range of alkenes [7]. Slippage of the rhodium fragment from an η^6 to η^4 to η^2 to even an η^0 bonding mode generates the necessary coordination sites required for catalysis. Upon completion of catalysis the ligand resumes a η^6 coordination, leaving the metal complex in a relatively stable resting state. Functionalized derivatives of catechol have also been used to make arylspiroboronate ester ligands, most notably pendant phosphine derivatives have been designed to coordinate to silver (Fig. 1d) [8].

Our interest in expanding the chemistry of these compounds led us to investigate the synthesis of a barium complex containing a bulky arylspiroboronate ester ligand. Barium compounds have found widespread applications in a number of areas, including solid state chemistry [9], metal ion sensors [10], electrolyte materials for fuel cells [11], biochemistry [12], and medicine [13].

*E-mails: *swestcott@mta.ca*
†adecken@unb.ca



Scheme 1. Synthesis of barium(II) bis{bis-(4,6-di-tert-butyl[1,2-benzenediolato(2-)-O,O']borate)}.

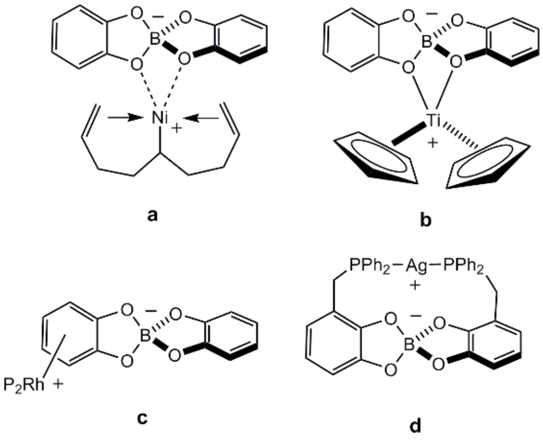


Figure 1. Metal complexes containing arylspiroboronate esters.

In this study we report our findings with the 3,5-di-*tert*-butylcatechol derivative to give the first structurally characterized barium arylspiroboronate ester complex.

2. Experimental Procedures

2.1. Materials and Measurements

Reagents and solvents were purchased from Aldrich Chemicals. NMR spectra were recorded on a JEOL JNM-GSX270 FT spectrometer. ^{1}H-NMR chemical shifts are reported in parts per million (ppm) and are referenced to residual solvent protons in deuterated solvent at 270 MHz. ^{11}B-NMR chemical shifts are reported in ppm and are referenced to BF_3•OEt_2 as an external standard at 87 MHz. ^{13}C-NMR chemical shifts are reported in ppm and are referenced to solvent carbon resonances at 68 MHz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), multiplet (m), overlapping (ov), and broad (br). Melting points were measured uncorrected with a Mel-Temp apparatus. Microanalyses for C, H, and N were carried out at Guelph Chemical Laboratories (Guelph, Ontario).

2.2. Synthesis

Barium(II) bis{bis-(4,6-di-tert-butyl[1,2-benzenediolato(2-)-O,O']borate)}

A stirred solution of 3,5-di-*tert*-butylcatechol (1.34 g, 6.0 mmol) in 15 mL of water was gently heated while a 10 mL solution of boric acid (188 mg, 3.0 mmol) in water was added dropwise. Barium hydroxide (257 mg, 1.5 mmol) was added directly to the solution as a solid and the mixture was heated at reflux for 8 hours then allowed to cool to room temperature. The resulting precipitate was collected by suction filtration, dissolved in hot hexane (10 mL) then stored at 5°C. The title compound precipitated as colourless crystals which were collected by suction filtration. Yield: 416 mg (28%); m.p. 204°C (decomposition). ^{1}H NMR (DMSO-D_6): ∂ 6.41 (s, 8H, Ar), 1.28 (s, 36H, CH_3), 1.21 (s, 36H, CH_3); ^{11}B NMR (THF): ∂ 13; ^{13}C{^{1}H} NMR (DMSO-D_6): ∂ 151.8, 147.5, 139.0, 128.7, 110.5, 104.4, 34.7, 34.2, 32.6, 30.1. Anal. calc. for $C_{56}H_{80}B_2BaO_8$ (1040.28) (%): C 64.65, H 7.76; found: C 64.65, H 7.50.

2.3. X-ray Crystallography

A single crystal of the barium compound was grown from a solution of acetone and water coated with Paratone-N oil, mounted using a polyimide MicroMount and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3 ° and 10 s exposure times. The detector distance was 5 cm. The data were reduced (SAINT) [14] and corrected for absorption (SADABS) [15]. The structure was solved by direct methods and refined by full-matrix least squares on F^2(SHELXTL) [16]. *Tert*-butyl groups were disordered but attempts to refine the positions of the methyl groups over two positions failed. The thermal parameters of the methyl groups are elongated as a result. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined using a riding model. Hydrogen atoms of water molecules were omitted.

3. Results and Discussion

In this study we have found that addition of 3,5-di-*tert*-butylcatechol and boric acid to barium hydroxide (Scheme 1) gave the formation of the first barium complex containing an arylspiroboronate ester ligand.

Table 1. Crystallographic data collection parameters for **1**.

Complex	**1**
CCDC deposit no.	762180
Formula	$C_{118}H_{196}B_4Ba_2O_{30}$
fw	2412.67
Crystal system	Triclinic
Space group	P-1
***a*, Å**	13.280(2)
***b*, Å**	15.755(3)
***c*, Å**	16.980(3)
***α*, deg**	71.691(2)
***β*, deg**	79.528(3)
***γ*, deg**	80.741(3)
***V*, Å^3**	3296.1(10)
Z	1
ρ_{calcd}, M g m^{-3}	1.215
Crystal size, mm^3	0.50 × 0.20 × 0.075
Temperature, K	173(1)
Radiation	MoKα (λ = 0.71073)
μ, mm^{-1}	0.661
Total reflections	23030
Total unique reflections	14370
No. of variables	720
R_{int}	0.0281
Theta range, deg	1.57 to 27.50
Largest difference peak/hole, e Å^{-3}	1.364/-1.103
S (GoF) on F^2	1.046
R1^a (I>2σ(I))	0.0434
wR2^b (all data)	0.1152

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR2 = (\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[wF_o^4])^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0528 * P)^2 + (1.4151 * P)]$ where $P = (\max(F_o^2, 0) + 2 * F_c^2)/3$.

In solution it is clear the boron remains four coordinate with a peak at ∂ 13 ppm in the ^{11}B NMR spectra. The catecholato groups appear to be equivalent in solution as only one peak in the ^1H NMR spectra is observed at ∂ 6.41 ppm using DMSO-d_6 as a solvent. This equivalency does not hold true in the solid state, however, the complex $\{(\eta^1\text{-}C_{28}H_{40}BO_4)_2Ba_2(\mu_2\text{-}H_2O)_2(H_2O)_8((CH_3)_2CO)_2(C_{28}H_{40}BO_4)_2\}$ (**1**)•$2H_2O$ can best be described as a barium dimer containing two bridging water molecules. A molecule of acetone and four terminal water molecules, along with coordination of one of the oxygen atoms (η^1) from one of the arylspiroboronate ester groups, provides each barium atom with a coordination number of eight (Fig. 2). The coordination chemistry of barium is well understood and coordination numbers (CN) from 3 to 12 have frequently been observed [17]. This material has two molecules of hydration per unit cell, but only one molecule of hydration per Ba atom.

Crystallographic data are given in Table 1 and selected bond distances and angles provided in Table 2. This compound is a rare structurally characterized example of a η^1 bound arylspiroboronate ester. While several examples of hydrogen bonded ammonium salts have been reported [6,18-21], the only other metal examples are those of lithium [1] and copper(I) [22] in which both metals are in the

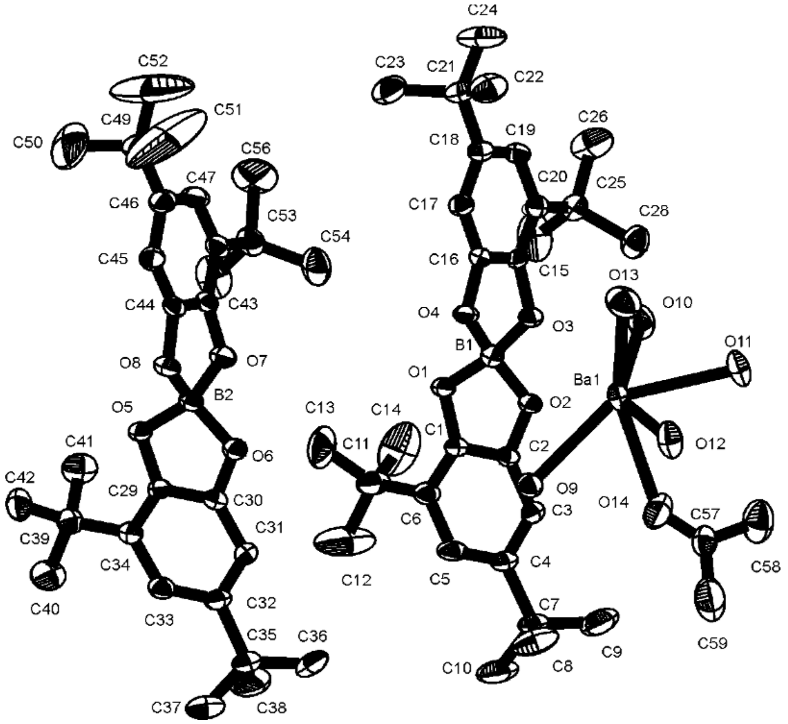


Figure 2. Molecular structure of the barium dimer $\{(\eta^1\text{-}C_{28}H_{40}BO_4)_2Ba_2(\mu_2\text{-}H_2O)_2(H_2O)_8((CH_3)_2CO)_2(C_{28}H_{40}BO_4)_2\}$ (1)•$2H_2O$ showing one of the barium atoms with 50% probability ellipsoids, the non-coordinating spiroboronate ester, hydrogen atoms and non-coordinating water molecules omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (o) for **1**.

Ba(1)-O(11)	2.700(2)
Ba(1)-O(12)	2.731(3)
Ba(1)-O(10)	2.738(3)
Ba(1)-O(14)	2.744(3)
Ba(1)-O(13)	2.768(3)
Ba(1)-O(9)#1	2.820(2)
Ba(1)-O(9)	2.843(2)
Ba(1)-O(2)	2.896(2)
Ba(1)-Ba(1)#1	4.7445(8)
B(1)-O(1)	1.452(4)
B(1)-O(3)	1.476(4)
B(1)-O(4)	1.498(5)
B(1)-O(2)	1.502(4)
B(2)-O(5)	1.470(4)
B(2)-O(7)	1.472(4)
B(2)-O(6)	1.485(4)
B(2)-O(8)	1.494(4)
O(11)-Ba(1)-O(12)	75.94(7)
O(11)-Ba(1)-O(10)	67.32(7)
O(12)-Ba(1)-O(10)	142.12(8)
O(11)-Ba(1)-O(14)	84.27(9)
O(12)-Ba(1)-O(14)	72.33(9)
O(10)-Ba(1)-O(14)	111.56(10)
O(11)-Ba(1)-O(13)	80.54(9)
O(12)-Ba(1)-O(13)	73.64(10)
O(10)-Ba(1)-O(13)	91.10(10)
O(14)-Ba(1)-O(13)	145.17(10)
O(11)-Ba(1)-O(9)#1	143.88(8)
O(12)-Ba(1)-O(9)#1	108.86(8)
O(10)-Ba(1)-O(9)#1	96.06(8)
O(14)-Ba(1)-O(9)#1	131.73(8)
O(13)-Ba(1)-O(9)#1	67.47(8)
O(11)-Ba(1)-O(9)	146.66(7)
O(12)-Ba(1)-O(9)	79.56(7)
O(10)-Ba(1)-O(9)	137.75(8)
O(14)-Ba(1)-O(9)	66.83(8)
O(13)-Ba(1)-O(9)	113.72(8)
O(9)#1-Ba(1)-O(9)	66.16(8)
O(11)-Ba(1)-O(2)	125.62(7)
O(12)-Ba(1)-O(2)	152.12(7)
O(10)-Ba(1)-O(2)	64.49(7)
O(14)-Ba(1)-O(2)	91.02(7)
O(13)-Ba(1)-O(2)	123.21(8)
O(9)#1-Ba(1)-O(2)	65.59(7)
O(9)-Ba(1)-O(2)	73.28(7)
O(1)-B(1)-O(3)	114.2(3)
O(1)-B(1)-O(4)	111.7(3)
O(3)-B(1)-O(4)	104.3(3)
O(1)-B(1)-O(2)	105.1(3)
O(3)-B(1)-O(2)	111.4(3)
O(4)-B(1)-O(2)	110.3(3)
O(5)-B(2)-O(7)	113.3(3)
O(5)-B(2)-O(6)	104.9(2)
O(7)-B(2)-O(6)	110.2(3)
O(5)-B(2)-O(8)	110.7(3)
O(7)-B(2)-O(8)	104.7(2)
O(6)-B(2)-O(8)	113.2(3)
C(1)-O(1)-B(1)	107.9(2)
C(2)-O(2)-B(1)	105.6(2)
C(2)-O(2)-Ba(1)	123.19(17)
B(1)-O(2)-Ba(1)	130.56(19)
Ba(1)#1-O(9)-Ba(1)	113.84(8)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+2

oxidation state of +1 and the arylspiroboronate esters coordinates via only one oxygen atom. The weakly bound arylspiroboronate ester has a barium oxygen distance of Ba(1)-O(2) 2.896(2) Å, which is slightly elongated compared to the distances observed for the bridging water molecules at 2.820(2) and 2.843(2) Å. The barium oxygen distances for the terminal water molecules are somewhat shorter at Ba(1)-O(10) 2.738(3), Ba(1)-O(11) 2.700(2) and Ba(1)-O(12) 2.731(3) Å. The B-O bond distances are typical for four coordinate boron catecholato groups [22]. It is interesting to note that the boron oxygen distance for the oxygen that is also involved in bonding to the barium atom is only slightly elongated at B(1)-O(2) 1.502(4) Å, compared to the B-O distances within the arylspiroboronate esters, with B(1)-O(1) 1.452(4), B(1)-O(3) 1.476(4) and B(1)-O(4) 1.498(5) Å, suggesting only a weak interaction with barium. By comparison, the boron oxygen distances for the adjacent non-coordinating (η^0) arylspiroboronate esters are B(2)-O(5) 1.470(4), B(2)-O(7) 1.472(4), B(2)-O(6) 1.485(4) and B(2)-O(8) 1.494(4) Å. Overall, the barium oxygen distances are typical for those observed in other barium complexes [24-27].

4. Conclusions

In summary, we have prepared and structurally characterized the first barium complex containing a bulky arylspiroboronate ester, observing a rare η^1 bonding mode for one of the boron groups. Further studies are currently underway to expand the coordination chemistry of these potentially versatile ligands and the results of which will be reported in due course.

Acknowledgements

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Supplementary Material

CCDC no. 762180 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/

retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, United Kingdom; fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.(1999)

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