### Synthesis and Structure of Boron–Bithiazole Complexes

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The syntheses of the first reported *p*-block complexes of the bithiazole moiety are reported, namely  $[(tBuBTz)BBr_2][Br]$ (3), and  $[(PhBTz)BBr_2][Br]$  (4) (tBuBTz = 4,4'-di-tert-butyl-2,2'-bithiazole and PhBTz = 4,4'-diphenyl-2,2'-bithiazole). Compounds 3 and 4 were prepared via reaction of equimolar

#### Introduction

The coordination chemistry of bithiazole ligands with transition metal elements is well established.<sup>[1]</sup> These neutral, four-electron, N-donor bidentate chelating ligands, have also found widespread use in materials chemistry as components in conjugated organic polymers.<sup>[2]</sup> The stereo-electronic properties of the ligand architecture are readily modified, for instance alkyl, carbocyclic or heterocyclic substituents are easily introduced in either the 4- or 5-positions (Figure 1).<sup>[3]</sup> It is thus surprising that the deployment of such a versatile ligand framework within the realm of s-block chemistry has been limited, and the *p*-block chemistry completely overlooked.



Figure 1. Numbering scheme of bithiazole ligand system.

In the present contribution we seek to redress this oversight by reporting the syntheses and molecular structures of two novel boron–bithiazole complexes. To the best of our knowledge these compounds represent the first examples of any *p*-block coordination complexes of the bithiazole moiety.

#### **Results and Discussion**

A considerable number of stable cationic boron complexes involving the interaction of monodentate Lewis bases quantities of the appropriate bithiazole ligand with  $BBr_3$ . The molecular structures of **3**, and the known compound PhBTz (**2**) were established using single-crystal X-ray diffraction techniques.

with alkyl- and haloboranes have been prepared and characterized.<sup>[4]</sup> The stabilities of these boronium complexes vary greatly depending on the nature of the Lewis base and the substituent on the boron atom. Despite the fact that the first stable cationic chelate boronium complex had been reported in 1906,<sup>[5]</sup> relatively few complexes involving neutral bi- and polydentate Lewis bases have been reported. Rund et al. prepared and characterized a series of complexes of the type [LLBX<sub>2</sub>][BX<sub>4</sub>], where X = F, Cl and LL = 1,10-phenanthroline, 2,2'-bipyridine.<sup>[6]</sup> Since these studies, a plethora of new chelating ligands containing diimine subunits have been disclosed, though surprisingly few examples remain structurally characterized.<sup>[4]</sup>

Crystals of **2**, suitable for X-ray diffraction studies, were grown from a concentrated chloroform solution at low temperature. Ligand **2** crystallized in the monoclinic space group C2/c and there are no unusually short intermolecular contacts. The thiazole rings are disposed in an overall *trans* fashion, consistent with previously described examples,<sup>[7]</sup> and the molecular structure is shown in Figure 2. Perhaps the most striking feature of **2** is the near co-planarity of the phenyl and bithiazole rings. The phenyl ring is twisted out of planarity by a mere 8.8°. Details of data collection and refinement are given in Table 1.



Figure 2. Molecular structure of PhBTZ (2). Selected bond lengths [Å] and angles [°]: C(1)–N(1) 1.302(2), N(1)–C(3) 1.384(2), C(3)–C(2)1.363(3), C(2)–S(1) 1.7086(18), S(1)–C(1) 1.7287(17), C(1)–N(1)–C(3) 110.55(14), N(1)–C(3)–C(2) 114.31(15), C(2)–S(1)–C(1) 88.64(8), S(1)–C(1)–N(1) 115.34(13).

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Compound	2	3
Formula	$C_{18}H_{12}N_2S_2$	$C_{14}H_{20}N_2S_2BBr_3$
Formula weight	320.42	530.98
Crystal system	monoclinic	triclinic
Space group	C2/c	PĪ
a /Å	18.7867(5)	10.4059(5)
b /Å	7.7364(2)	12.9470(5)
c /Å	11.4354(3)	16.7728(7)
a /°	90	83.200(2)
β /°	116.127(2)	78.822(2)
γ /°	90	74.700(3)
$V/Å^3$	1492.21(7)	2132.87(16)
Ζ	4	4
$\rho_{\rm calcd.}  [\rm g  cm^{-1}]$	1.426	1.654
F(000)	664	1040
Crystal size /mm	$0.25 \times 0.10 \times 0.10$	$0.10 \times 0.20 \times 0.10$
$\theta$ range [°]	6.29-66.50	2.69-66.05
Number of reflections	6514	7045
collected		
Independent reflections	1309	6226
$R_1 \left[I > 2\sigma(I)\right]$	0.0314	0.0531
$wR_2$ (all data)	0.0868	0.1352
Peak and hole [eÅ <sup>-3</sup> ]	0.396 and -0.189	0.356 and -0.167

Table 1. Crystal structure determination of 2 and 3.

In order to gain additional insight into the electronic structure of ligand **2**, DFT calculations were carried out at the B3LYP level of theory<sup>[8]</sup> using the Gaussian 03 suite of programs.<sup>[9]</sup> The fractional coordinates from the X-ray crystal structure was used as input data. The  $6-31G^*$  basis set was employed for all elements. In general, there is a very good agreement between the theoretical and experimental values. For example, the computed C=N bond length of 1.305 Å compares well with the experimental value of 1.302(2) Å. Furthermore, the examination of the HOMO of **2** revealed extensive delocalization throughout the ligand framework, thus explaining the origin of the near co-planarity of the phenyl and thiazole rings.

Reaction of either *t*BuBtz (1) or PhBtz (2) with BBr<sub>3</sub> (1 equiv.) in dichloromethane solution affords, after work up, the cationic bithiazole complexes **3** and **4**, respectively (Scheme 1). These salts are isolated as yellow powders in nearly quantitative yields. Characteristic, four-coordinate, <sup>11</sup>B NMR signals were observed for both **3** and **4** ( $\delta = 11.23$ , and 4.76 ppm, respectively).<sup>[10]</sup> Both <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR studies indicate that an overall  $C_{2\nu}$  symmetric structure is retained in solution. Crystals of **3** suitable for an X-ray diffraction study were grown from dichloromethane solution at -40 °C.

Boronium cation 3 crystallizes in the triclinic space group  $P\bar{1}$  and the solid-state structure consists of arrays of individual molecules with no unusually short intermolecular contacts. The molecular structure is depicted in Figure 3 (a) and data collection/refinement details are presented in Table 1. The closest contact between the outer sphere bromide and the boron center is 5.612 Å and thus exceeds the sum of the van der Waals radii for boron and bromine (4.0 Å). In contrast to closely related diimine-supported  $[BX_2]^+$  cations,<sup>[11]</sup> the five-membered ring formed by chelation of the  $[BBr_2]^+$  is not planar, with the boron center





Scheme 1. Preparation of complexes 3 and 4.

puckered out of the plane by 0.195 Å. The average B–N, N–C<sub>imino</sub> and C–C<sub>ring</sub> bond lengths are 1.581(9), 1.335(9), and 1.360(10) Å, respectively, thus indicating retention of the N=C imino linkages and binding of the nitrogen atoms in a purely dative fashion. Intriguingly, upon close examination of the extended packing of monomers a weak interaction between the outer-sphere bromide ion and chelating sulfurs of the ligand framework was evident. This interaction (3.577 Å), illustrated in Figure 3 (b), falls within the



Figure 3. (a) Molecular structure of **3**. Selected bond lengths [Å] and angles [°]: C(1)-N(1) 1.324(9), C(4)-N(2) 1.347(9), C(2)-C(3) 1.370(10), C(5)-C(6) 1.351(9), C(1)-C(4) 1.446(10), C(1)-S(1) 1.683(7), S(1)-C(3) 1.716(7), C(4)-S(2) 1.682(7), S(2)-C(6) 1.714(6) N-B(av.) 1.581(9), B–Br(av.) 1.989(7), C(1)-N(1)-C(2) 112.0(5), C(4)-N(2)-C(5) 110.7(5), C(1)-S(1)-C(3) 88.1(4), C(4)-S(2)-C(6) 87.6(3), S(1)-C(1)-N(1) 116.2(5), S(2)-C(4)-N(2) 116.2(5), N(1)-B(1)-N(2) 99.2(5). (b) Interaction of outer sphere bromine ion with sulfur-chelate.



sum of the van der Waals radii of sulfur and bromine (3.65 Å). Such an interaction raises the possibility of using the sulfur chelate to coordinate a second metal center and current efforts are focused at the introduction of gold centers, for instance.

DFT calculations were carried out on the cation **3** at an identical level of theory as indicated above. The computed charge (Mulliken) at the boron center is +0.504. This partial quenching of charge at a boronium cation by donor ligands is observed for both borenium and boronium systems.<sup>[4]</sup> However, as noted recently,<sup>[12]</sup> care should be taken in the interpretation of such charge values and more extensive electronic structure calculations are currently being undertaken.

#### Conclusions

The first coordination complexes of the bithiazole ligand class with boron have been prepared and characterized. The boron complexes [(*t*BuBTz)BBr<sub>2</sub>][Br], and [(PhBTz)BBr<sub>2</sub>]-[Br] could be easily obtained by treatment of the appropriate bithiazole ligand with an equimolar quantity of BBr<sub>3</sub>. The molecular structure of the novel boronium cation **3**, obtained via boron–bromine bond heterolysis, was determined using single-crystal X-ray diffraction experiments. Further studies are currently underway to expand the scope of the main-group coordination chemistry of this hitherto neglected ligand class.

### **Experimental Section**

General Procedures: All manipulations were carried out using standard vacuum, Schlenk, cannula or glovebox techniques. Argon gas was purified by passage through columns of BASF R3–11 and 4-Å molecular sieves. THF was distilled from sodium benzophenone ketyl under nitrogen. Deuterated solvents were purchased from Cambridge Isotope Laboratories and dried with 4-Å molecular sieves ([D<sub>6</sub>]benzene, [D<sub>2</sub>]dichloromethane) and distilled prior to use. Methylene chloride was dried with CaH<sub>2</sub> and distilled prior to use. All other reagents were purchased from Aldrich, or Acros chemicals and used as received.

**Physical Measurements:** High-resolution ESI mass spectra were recorded on a Bruker Daltonics, Inc., Billerica, MA, USA, BioToF instrument. All analyses were performed on samples that had been sealed in glass capillaries under an argon atmosphere. <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR spectra were recorded on DRX 400 and 500 MHz spectrometers. <sup>1</sup>H and <sup>13</sup>C chemical shifts are referenced to residual solvent signals; <sup>11</sup>B chemical shifts are referenced to an external standard of BF<sub>3</sub>·OEt<sub>2</sub>.

**X-ray Crystallography:** For compounds **2**, and **3** a crystal of suitable quantity was removed from a Schlenk flask under positive argon pressure, covered immediately with degassed hydrocarbon oil and mounted on a glass fiber. The X-ray diffraction data were collected at 173 K on a Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream low-temperature device and a graphite-monochromated Mo- $K_a$  radiation source ( $\lambda = 0.71973$  Å). Corrections were applied for Lorentz and polarization effects. All structures were solved by direct methods<sup>[13]</sup> and refined by full-matrix least-squares cycles on  $F^2$ . All non-hydrogen atoms were allowed

anisotropic thermal motion, and hydrogen atoms were placed in fixed, calculated positions using a riding model (C–H: 0.96 Å). Selected crystal data, and data collection and refinement parameters are listed in Table 1. Elemental analyses were performed by Robertson Microlit Laboratories Inc. in Madison, NJ.

CCDC-750087 (for 2) and -750088 (for 3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

**4,4'-Di-tert-butyl-2,2'-bithiazole (1):** Following a literature procedure,<sup>[14]</sup> a mixture of 1-bromopinacolone (3.759 g, 21 mmol), dithioxamide (1.202 g, 10 mmol) and ethanol (60 cm<sup>3</sup>) was refluxed for 4 h to afford a red supernatant liquid with a pale solid mixture. After cooling, the reaction mixture was placed in a freezer (–40 °C) and left overnight. The pale yellow solid was isolated via filtration and dried under reduced pressure (2.200 g, 79%). Spectroscopic characterization was in agreement with literature values.

**4,4'-Diphenyl-2,2'-bithiazole (2):** Using a similar procedure as above, **2** was prepared in 80% yield from 2-bromoacetophenone. Crystals suitable for study via X-ray diffraction experiments were grown from concentrated chloroform solutions. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 7.97$  (d, J = 7.2 Hz, 4 H, aryl *ortho*); 7.58 (s, 2 H, thiazole CH); 7.45 (t, J = 14.8 Hz, 4 H, aryl *meta*); 7.36 (t, J = 7.2 Hz, 2 H, aryl *para*) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75.5 MHz):  $\delta = 161.3$  (thiazole, C-thiazole); 156.7 (C-Ph); 134.0 (Ph); 128.8 (Ph); 128.5 (Ph); 126.5 (Ph, C2); 114.7 (thiazole, C-H) ppm. HRMS: expected [M + H]+ 321.0523, observed 321.0520.

**Preparation of [(***t***BuBtz)BBr<sub>2</sub>[[Br] (3):** To a dichloromethane (10 cm<sup>3</sup>) solution of 1 (280 mg, 1 mmol), was added boron tribromide as a dichloromethane solution (1 cm<sup>3</sup>, 1.0 M) at ambient temperature. The yellow solution was allowed to stir at this temperature for 12 h before the solvent was removed under reduced pressure to yield **3** as a free flowing yellow powder (501 mg, 95%). Crystals suitable for study by X-ray diffraction were grown from concentrated dichloromethane solutions at -30 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz): δ = 7.55 (s, 2 H, thiazole CH); 1.56 [s, 18 H, (CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75.5 MHz): δ = 164.3 (thiazole, C=N); 159.5 (thiazole, C–C); 114.7 (thiazole, C–H); 35.4 (*t*Bu); 29.5 (*t*Bu) ppm. <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>, 96 MHz): δ = 11.23 (s) ppm. HRMS: expected [M<sup>+</sup>] 450.9507, observed 450.9510. C<sub>14</sub>H<sub>20</sub>BBr<sub>3</sub>N<sub>2</sub>S<sub>2</sub>·C<sub>7</sub>H<sub>8</sub> (623.11): calcd. C 40.48, H 4.53; found C 40.86, H 5.03.<sup>[15].</sup>

**Preparation of [(PhBtz)BBr<sub>2</sub>][Br] (4):** Compound **4** was prepared in 85% yield from **2** in a manner similar to that described above. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz):  $\delta$  = 8.09 (d, *J* = 7.0 Hz, 4 H, aryl *ortho*), 7.87 (s, 2 H, thiazole CH), 7.55 (t, *J* = 15.5 Hz, 4 H, aryl *meta*), 7.36 (m, 2 H, aryl *para*) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75.5 MHz):  $\delta$  = 162.4 (thiazole, C-thiazole), 156.3 (thiazole, C-Ph), 134.0 (Ph), 128.2 (Ph), 127.9 (Ph), 125.5 (Ph), 116.2 (thiazole, CH) ppm. <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>, 96 MHz):  $\delta$  = 4.76 (s) ppm. HRMS: expected [M<sup>+</sup>] 490.8881, observed: 490.8903. C<sub>18</sub>H<sub>12</sub>BBr<sub>3</sub>N<sub>2</sub>S<sub>2</sub>·C<sub>7</sub>H<sub>8</sub> (663.09): calcd. C 45.28, H 3.04; found C 45.21, H 3.27.<sup>[15]</sup>

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