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π -Bonding in B–O ring species: Lewis acidity of $\text{Me}_3\text{B}_3\text{O}_3$, synthesis of amine $\text{Me}_3\text{B}_3\text{O}_3$ adducts, and the crystal and molecular structure of $\text{Me}_3\text{B}_3\text{O}_3\cdot\text{NH}_2^i\text{Bu}\cdot\text{MeB}(\text{OH})_2$

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Received 2 February 1999; received in revised form 19 March 1999

Abstract

The synthesis and characterisation (m.p., elemental analysis, IR, NMR) of some previously unreported $\text{Me}_3\text{B}_3\text{O}_3\cdot\text{L}$ adducts (L = piperidine, isobutylamine, morpholine, 3-picoline, benzylamine) are described. The crystal and molecular structure of $\text{Me}_3\text{B}_3\text{O}_3\cdot\text{NH}_2^i\text{Bu}\cdot\text{MeB}(\text{OH})_2$ has been determined by a single-crystal X-ray diffraction study. The structure reveals an unusual H-bond interaction between $\text{MeB}(\text{OH})_2$ and a ring O atom of the six-membered B_3O_3 ring of the trimethylboroxine adduct, $\text{Me}_3\text{B}_3\text{O}_3\cdot\text{NH}_2^i\text{Bu}$. The direction of the H-bond strongly suggests sp^2 hybridisation for this O atom. The Lewis acidity of $\text{Me}_3\text{B}_3\text{O}_3$, $\text{Ph}_3\text{B}_3\text{O}_3$, 1,3,5- $\text{Ph}_3\text{B}_3\text{N}_3\text{Me}_3$ and 1,3,5- $\text{Ph}_3\text{C}_6\text{H}_3$ have been estimated by Gutmann's method and data interpreted in terms of relative π -bonding strength within these ring systems. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Boron; Boroxine; Lewis acidity; X-ray structure

1. Introduction

B–O π -bonding in boroxines ($\text{R}_3\text{B}_3\text{X}_3$) ($\text{X} = \text{O}$) and the extent of aromaticity in these and related six-membered ring systems ($\text{X} = \text{NR}$, PR , S) has been open to considerable debate in the literature [1]. Structural studies [2–6] of compounds containing the boroxine ring confirm its planar nature, and also confirm that the B–O bond lengths within the ring are equivalent (~ 1.38 Å) and at a distance generally shorter than that observed for a B–O single bond (~ 1.46 Å); the B–O–B angles ($\sim 120^\circ$) are also indicative of aromatic π -bonding. However, magnetic

[7], magneto-optical [8], NMR [9] and computational evidence [1] suggest the aromatic character of boroxines is weaker than that of borazenes with the 'p-electrons' being considerably localised at oxygen as lone pairs. In order to maximise aromatic π -interaction in boroxines the oxygen atoms must be sp^2 hybridised, with lone pairs in the π (p) orbitals and *exo*- sp^2 hybrids. However, the exact location of their lone pairs is unknown. In the related borazenes, the sp^2 nature of the nitrogen atoms is confirmed by three co-planar substituents at each of the nitrogen atoms. We here report the synthesis and spectroscopic properties of a series of ligand adducts of $\text{Me}_3\text{B}_3\text{O}_3$ and the crystal and molecular structure of a derivative of one of these, $\text{Me}_3\text{B}_3\text{O}_3\cdot\text{NH}_2^i\text{Bu}\cdot\text{MeB}(\text{OH})_2$; the latter provides evidence in support of the hybridisation of an annular oxygen atom as sp^2 . Gutmann's method [10,11] has been used to estimate the Lewis acidity of $\text{R}_3\text{B}_3\text{O}_3$ ($\text{R} = \text{Me}$ and Ar) and the data obtained are compared with data obtained for related 1,3,5- $\text{Ph}_3\text{C}_6\text{H}_3$ and 1,3,5- $\text{Ph}_3\text{B}_3\text{N}_3\text{Me}_3$.

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2. Results and discussion

$\text{Me}_3\text{B}_3\text{O}_3$ and its 1:1 amine adducts, $\text{Me}_3\text{B}_3\text{O}_3\cdot\text{L}$ ($\text{L} = \text{NH}_3, \text{NMe}_3$) are documented [12–14] and a convenient reported preparation of $\text{Me}_3\text{B}_3\text{O}_3$ from $\text{B}(\text{OMe})_3$ involves the synthesis and subsequent de-ligation of $\text{Me}_3\text{B}_3\text{O}_3\cdot\text{py}$ [15]. The reaction of $\text{Me}_3\text{B}_3\text{O}_3$ with a stoichiometric quantity of amine in Et_2O solution at room temperature afforded $\text{Me}_3\text{B}_3\text{O}_3\cdot\text{L}$ ($\text{L} = \text{piperidine}$, **1**; isobutylamine, **2**; morpholine, **3**; 3-picoline, **4**; benzylamine, **5**) in excellent yield. Compounds **1–5** were air-stable, colourless/white crystalline solids and were characterised by their m.p. and elemental analysis (Table 1), and by (solution) NMR and IR spectroscopy (Table 2). Amine adducts of $\text{Et}_3\text{B}_3\text{O}_3$ [16] and $\text{Ar}_3\text{B}_3\text{O}_3$ [6,17–20] have been shown to undergo in solution a temperature-dependent fluctuation of the amine between the three borons of the boroxine ring and this has been attributed to a ligand dissociation–recombination (exchange) process which is generally ‘fast’ at room temperature. The ^1H -NMR data for **1–5** at room temperature are all consistent with this, with only one signal [ca. 0.0 ppm (9H)] observed for the B–Me protons of the boroxine rings. Variable temperature ^1H -NMR (250 MHz) for **1** in CD_2Cl_2 indicated that the process could be ‘slowed’ and at 203 K two signals [–0.3 ppm (3H), +0.15 (6H)] were observed; upon warming these signals coalesced at 213 K. Variable temperature ^{11}B - ^1H spectra (80.25 MHz) were also obtained for **1** which showed two signals [+32.4 (2B), +6.0 (1B) ppm] at 253 K; coalescence of these signals occurred upon warming to 258 K, and further warming gave a singlet at 293 K [+22.1 ppm]. From these data ΔG^\ddagger was calculated [21,22] to be ca. $43 \pm 2 \text{ kJ mol}^{-1}$ and at the lower end of the range observed (39–54 kJ mol^{-1} [19]) for related processes. Unfortunately, ΔG^\ddagger for the compounds **2–5** were not obtained since low-temperature limiting ^1H spectra were not observed (even at 183 K) and the ^{11}B - ^1H signals were generally so broadened at lower temperature as to be effectively lost in the base-line noise. It has been suggested that disruption of the boroxine π -system may dominate the energetics of this ligand dissociation–recombination process since neither steric nor electronic effects can be correlated with variations of ΔG^\ddagger values [19].

The compound $\text{Me}_3\text{B}_3\text{O}_3\cdot\text{NH}_2^i\text{Bu}\cdot\text{MeB}(\text{OH})_2$ (**6**) was obtained as a crystalline decomposition product from an attempted prolonged recrystallisation of **2** from $\text{CHCl}_3/40\text{--}60^\circ\text{C}$ petroleum ether; the appearance of $\text{MeB}(\text{OH})_2$ in the crystalline material presumably arose from partial hydrolysis of **2** caused by adventitious water in the recrystallisation solvents. Compound **6** crystallised with two independent molecules within the asymmetric fraction of the unit cell. ORTEP drawings of both of the molecules are shown in Fig. 1; selected bond distances and angles given in Table 3. The discussion in this section is limited to molecule A whilst molecule B has similar overall dimensions but differs in the conformation of the *iso*-butyl group on the amine ligand. Compound **6** is derived from **2** and as such contains a six-membered alternating B_3O_3 ring, similar to the starting boroxine system, with an additional co-ordinate bond from the nitrogen atom [N(01)] to one of the three boron atoms [B(3)]. Internuclear angles at 4-coordinate B(3) range from 105.8 to 113.6°, consistent with a distorted tetrahedral geometry and sp^3 hybridisation, whilst B(1) and B(2) remain trigonal-planar 3-coordinate (sp^2 hybridised) with internuclear angles 118.4–121.5° [Σ at B(1) 360.0°, Σ at B(2) 360.0°]. An unusual and unique feature of **6** is that whilst two of the oxygen atoms [O(1) and O(3)] are 2-coordinate the third oxygen [O(2)] is 3-coordinate by a H-bonding interaction with a co-crystallised molecule of $\text{MeB}(\text{OH})_2$. This is the first documented example of a cyclic B_3O_3 ring system showing Lewis basicity at O; presumably it occurs in **6** because the ring system is now relatively electron-rich as a consequence of adduct formation. The H atom [H(01)] was located and H-bonding interaction is relatively strong [H(01)⋯O(2), 1.859 Å]. Furthermore, the hydrogen atom [H(01)] is essentially co-planar with the B_3O_3 ring [H(01)–O(2)–B(1)–O(1), dihedral angle 175.2°] and the H(01)–O(2)–B(1), H(01)–O(2)–B(3), and B(1)–O(2)–B(3) angles are, respectively, 124.3, 110.9 and 124.4(3)° [$\Sigma = 359.6^\circ$], confirming the sp^2 hybridisation of O(2). The smaller H(01)–O(2)–B(3) angle is entirely consistent with VSEPR theory [23] and the increased repulsive forces involved in a O(2)–B(1) π -interaction. The effect of this H-bond interaction upon the other dimensions within the structure is minimal with B–O–B and

Table 1
Yields, m.p. and elemental analysis data for amine adducts $\text{Me}_3\text{B}_3\text{O}_3\cdot\text{L}$ (**1–5**)^a

$\text{Me}_3\text{B}_3\text{O}_3\cdot\text{L}$ adduct L =	Yield	m.p. (°C)	C	H	N
1 Piperidine	95	164–168	45.5(45.6)	9.4(9.6)	6.7(6.65)
2 Isobutylamine	92	150–154	42.35(42.3)	10.2(10.15)	7.0(7.05)
3 Morpholine	94	160–165	39.7(39.7)	8.2(8.1)	6.7(6.6)
4 3-Picoline	91	52–56	49.5(49.4)	7.2(7.4)	6.4(6.4)
5 Benzylamine	96	140–144	51.8(51.6)	6.2(6.0)	7.7(7.7)

^a Calculated in parentheses.

Table 2
IR and NMR (^1H , ^{11}B , ^{13}C) data for amine adducts $\text{Me}_3\text{B}_3\text{O}_3\cdot\text{L}$ (**1–5**)

	$\delta(^{11}\text{B})$ (ppm) ^a	$\nu(\text{BO})$ ^b (cm^{-1})	$\delta(^1\text{H})$ (ppm)	$\delta(^{13}\text{C})$ (ppm)
1	22.1	1406, 1360, 1330, 1308, 1288, 1240	0.0 (s, 9H), 1.5 (m, 6H), 2.55 (br s, 1H), 2.8 (m, 4H)	1.5, 23.1, 25.3, 44.9
2	21.6	1388, 1331, 1270, 1248	0.0 (s, 9H), 0.85 (d, 6H), 1.7 (m, 1H), 2.45 (d, 2H), 3.9 (br s, 2H)	2.2, 20.0, 28.1, 46.7
3	22.0	1420, 1389, 1336, 1305, 1276, 1253	0.0 (s, 9H), 2.8 (t, 4H), 3.3 (br s, 1H), 3.65 (t, 4H)	1.5, 43.8, 65.9
4	22.8	1374br, 1277	0.2 (s, 9H), 2.5 (s, 3H), 7.5 (t, 1H), 7.8 (d, 1H), 8.4 (s, 1H), 8.5 (d, 1H)	3.2, 18.7, 124.9, 135.8, 140.8, 141.0, 143.6
5	22.2	1363br, 1271, 1244	0.0 (s, 9H), 3.65 (s, 2H), 4.4 (br s, 2H), 7.25 (m, 5H)	2.1, 43.8, 128.1, 128.7, 129.3, 136.0

^a Recorded at room temperature in CDCl_3 .

^b Obtained as KBr discs.

O–B–O ring angles, and B–O bond lengths within the expected ranges for 1:1 boroxine:amine adducts and with bond distances and angles involving O(2) being not significantly different to those of the non-H-bonded, but otherwise chemically equivalent O(3). The variations of B–O bond lengths within this adduct have been previously noted for other adducts [6,18–20] and are clearly due to the increased co-ordination number of B(3), resulting in loss of π -bonding in the two B–O bonds involving this boron and a redistribution of π -electron density around the remaining atoms of the ring.

Gutmann and co-workers have described a quantitative parameter (acceptor number, AN) which is derived from variations of the ^{31}P -NMR chemical shift obtained for Et_3PO by electrophilic solvent interactions [10,11]; the AN scale has arbitrary fixed points for hexane (0) and SbCl_5 (100). In relation to the Lewis acidity of trigonal boron compounds, the AN value is a measure of how well the O donor atom of the Et_3PO competes with the substituents bound to boron for its acceptor orbital; in unsaturated six-membered ring systems Lewis acidity would be expected to be reduced by strong (aromatic) π -bonding. An AN of 51 was determined for $\text{Me}_3\text{B}_3\text{O}_3$ by Gutmann's method and comparable ANs of 49, 50, and 52 were estimated for the solid boroxines $\text{Ar}_3\text{B}_3\text{O}_3$ (Ar = Ph; 4- BrC_6H_4 ; 3- $\text{NO}_2\text{C}_6\text{H}_4$) by a modified 'solution-method' [24]. The Lewis acidities of these alkyl/aryl boroxines are considerable but lower than that of metaborate esters (65–80) which are significantly stronger Lewis acids (cf. BF_3 , AN = 89) [24]. These lower acidities may be attributed to a number of factors, which include the reduction of the average of the electronegativities of the elements directly bound to boron, strong hyperconjugation of Me to B, and/or stronger heterocyclic ring π -bonding. For comparison, the ANs of the related solids 1,3,5- $\text{Ph}_3\text{B}_3\text{N}_3\text{Me}_3$ and 1,3,5- $\text{Ph}_3\text{C}_6\text{H}_3$ were estimated to be 21 and < 13, respectively. Although again inductive electronegativity effects may dominate the ANs, the

order of data is consistent with previous observations [1–9] and indicates that π -bonding decreases in the series 1,3,5- $\text{Ph}_3\text{C}_6\text{H}_3$ > 1,3,5- $\text{Ph}_3\text{B}_3\text{N}_3\text{Me}_3$ > $\text{Ar}_3\text{B}_3\text{O}_3$. The higher Lewis acidity of boroxines relative to borazenes is reflected in the ability of the former to form isolatable adducts.

To conclude, structural evidence has been obtained which indicates that the B atoms in boroxine rings are hybridised in such a way as to maximise possible B–O π -bonding but Lewis acidity measurements on these boroxines indicate that any such π -interactions are weaker than those observed in the related borazenes.

3. Experimental

3.1. General

Reactions were carried under standard Schlenk techniques under N_2 and all solvents were dried before use. IR spectra were recorded on a Perkin–Elmer FT-IR 1600 spectrometer as KBr discs. Multi-element NMR spectra were recorded on a Bruker AC CP/MAS NMR spectrometer operating at 250 MHz for ^1H , 62.9 MHz for ^{13}C - $\{^1\text{H}\}$, 80.25 MHz for ^{11}B - $\{^1\text{H}\}$, and 101.25 MHz for ^{31}P - $\{^1\text{H}\}$. $\text{Me}_3\text{B}_3\text{O}_3$, piperidine, isobutylamine, morpholine, 3-picoline, benzylamine, were obtained commercially and distilled immediately before use. 1,3,5- $\text{Ph}_3\text{C}_6\text{H}_3$ and Et_3PO were obtained commercially. 1,3,5- $\text{Ph}_3\text{B}_3\text{N}_3\text{Me}_3$ was prepared by a literature method [25].

The complexes **1–5** were all prepared by the same method as described below for **3**. A few crystals of **6**, suitable for single-crystal X-ray diffraction analysis, were obtained as a decomposition product from an attempted prolonged recrystallisation of **2** from CHCl_3 /40–60°C petroleum ether at room temperature [$\text{C}_8\text{H}_{25}\text{NO}_5\text{B}_4$: (**6**): Calc. C 37.2, H 9.75, N 5.4; Found C 37.5, H 9.45, N 5.5; m.p. 134–138°C; IR: 3422 cm^{-1} $\nu(\text{OH})$, 1384 cm^{-1} $\nu(\text{BO})$, 1118 cm^{-1}].

3.2. Synthesis of **3**

To $\text{Me}_3\text{B}_3\text{O}_3$ (0.5 g, 4.0 mmol) in Et_2O (20 ml) at room temperature was added morpholine (0.35 g, 4.0 mmol) in Et_2O (20 ml). The solution was allowed to stir for 10 mins and then evaporated to dryness to afford the product (0.8 g, 94%) as a microcrystalline analytically pure sample.

3.3. Lewis acidity

Measurements were made as described previously [24] and AN values were calculated using $\text{AN} = 2.2(\delta^{31}\text{P} - 41)$ from the following ^{31}P -NMR data of Et_3PO in solution as follows: neat $\text{Me}_3\text{B}_3\text{O}_3$ (δ 64.3); 0.61 M $\text{Ph}_3\text{B}_3\text{O}_3$ in THF (δ 63.2); 3.6 M (4- BrC_6H_4) $_3\text{B}_3\text{O}_3$ in DMSO (δ 63.8); 3.6 M (3- $\{\text{NO}_2\}\text{C}_6\text{H}_4$) $_3\text{B}_3\text{O}_3$ in DMSO (δ 64.8); 0.97 M 1,3,5- $\text{Ph}_3\text{C}_6\text{H}_3$ in THF (δ 46.9); 0.92 M 1,3,5- $\text{Ph}_3\text{B}_3\text{N}_3\text{Me}_3$ in THF (δ 50.7).

3.4. X-ray structure of **6**

A colourless crystal of dimensions $0.3 \times 0.3 \times 0.2$ mm was selected for X-ray work. Cell dimensions and intensity data were recorded at 150 K, as previously described [26] using a FAST TV area detector diffractometer mounted at the window of a rotating anode operating at 50 kV, 50 mA with a molybdenum anode ($\lambda(\text{Mo-K}\alpha) = 0.71069 \text{ \AA}$). The crystal-to-detector distance was 50 mm and the detector 2θ swing angle was 20° . Slightly more than one hemisphere of data

was recorded. Following normal data processing, the space group was determined as $P2_1/c$ from analysis of the systematically absent reflections. The structure was solved via direct methods [27] and refined by full matrix least squares [28]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions, except those of the –OH groups which were located from the difference map and refined. Refinement was based on F^2 , and involved a total of 354 parameters. Crystal data for $\text{C}_8\text{H}_{25}\text{NO}_5\text{B}_4$ (**6**): $M = 517.06$, crystal size $0.3 \times 0.3 \times 0.2$ mm, monoclinic, space group $P2_1/c$, $a = 9.342(2)$, $b = 22.300(4)$, $c = 15.935(3) \text{ \AA}$, $\beta = 106.49(3)^\circ$, $Z = 8$, $U = 3183.1(11)$, $T = 150(2) \text{ K}$, $D_c = 1.079 \text{ Mg m}^{-3}$, $\lambda = 0.71069 \text{ \AA}$, 7236 reflections, 4260 independent [$I > 2\sigma(I)$] ($R_{\text{int}} = 0.094$), $\theta_{\text{max}} = 25.08^\circ$, $R_1 = 0.0914$, $wR_2 = 0.1468$ for all data. $R_1 = \Sigma(\Delta F)/\Sigma(F_o)$, $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = \{\sigma^2[F_o^2]\}^{-1}$.

4. Supplementary material

Fractional coordinates, anisotropic displacement coefficients, full lists of bond lengths and angles, hydrogen atom parameters, and structure factor tables are deposited with the Cambridge Crystallographic Data Centre, CCDC No. 111537. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

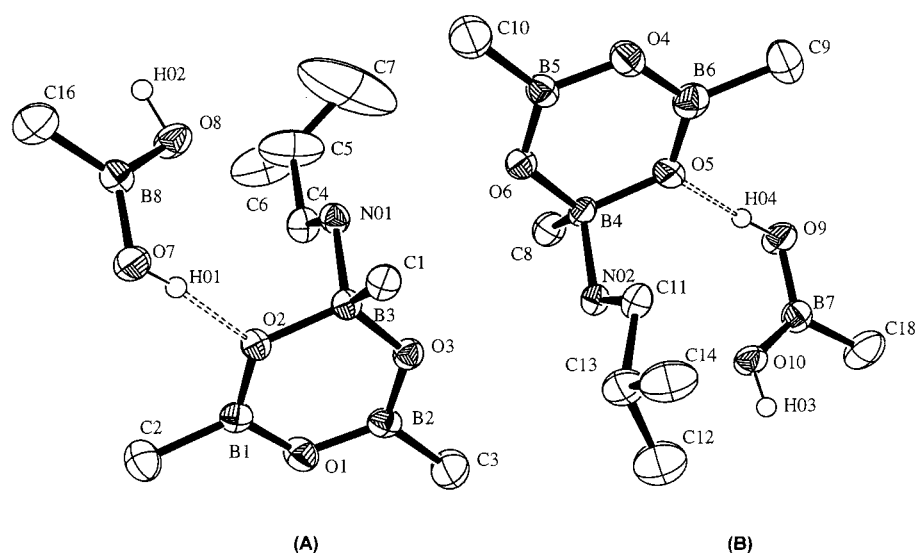


Table 3
Selected internuclear distances and angles for $\text{Me}_3\text{B}_3\text{O}_3 \cdot \text{NH}_2\text{Bu-MeB}(\text{OH})_2$ (6)

Molecule (A)		Molecule (B)	
<i>Bond distances</i> (Å)			
B(1)–O(2)	1.347(4)	B(6)–O(5)	1.356(5)
O(2)–B(3)	1.482(4)	O(5)–B(4)	1.479(4)
B(3)–O(3)	1.475(4)	B(4)–O(6)	1.467(4)
O(3)–B(2)	1.351(4)	O(6)–B(5)	1.343(4)
B(2)–O(1)	1.379(4)	B(5)–O(4)	1.376(4)
O(1)–B(1)	1.397(4)	O(4)–B(6)	1.390(5)
B(8)–O(7)	1.366(4)	B(7)–O(9)	1.371(4)
B(8)–O(8)	1.373(4)	B(7)–O(10)	1.369(5)
N(01)–B(3)	1.618(4)	N(02)–B(4)	1.627(4)
B(3)–C(1)	1.592(5)	B(4)–C(8)	1.596(5)
B(2)–C(3)	1.563(5)	B(5)–C(10)	1.575(5)
B(1)–C(2)	1.562(5)	B(6)–C(9)	1.560(5)
B(8)–C(16)	1.547(5)	B(7)–C(18)	1.547(5)
C(4)–N(01)	1.490(4)	C(11)–N(02)	1.490(4)
<i>Bond angles</i> (°)			
O(1)–B(1)–O(2)	119.1(3)	O(4)–B(6)–O(5)	119.0(3)
O(2)–B(3)–O(3)	111.3(3)	O(5)–B(4)–O(6)	111.5(3)
O(3)–B(2)–O(1)	120.6(3)	O(6)–B(5)–O(4)	120.7(3)
B(1)–O(2)–B(3)	124.4(3)	B(6)–O(5)–B(4)	123.9(3)
B(3)–O(3)–B(2)	123.3(3)	B(4)–O(6)–B(5)	123.5(3)
B(2)–O(1)–B(1)	121.2(3)	B(5)–O(4)–B(6)	121.3(3)
C(1)–B(3)–N(01)	108.4(3)	C(8)–B(4)–N(02)	107.9(3)
C(1)–B(3)–O(2)	112.2(3)	C(8)–B(4)–O(5)	112.2(3)
C(1)–B(3)–O(3)	113.6(3)	C(8)–B(4)–O(6)	113.8(3)
N(01)–B(3)–O(3)	105.4(2)	N(02)–B(4)–O(6)	105.8(2)
N(01)–B(3)–O(2)	105.3(2)	N(02)–B(4)–O(5)	105.0(2)
C(3)–B(2)–O(3)	121.0(3)	C(10)–B(5)–O(6)	121.7(3)
C(3)–B(2)–O(1)	118.4(3)	C(10)–B(5)–O(4)	117.6(3)
C(2)–B(1)–O(1)	119.4(3)	C(9)–B(6)–O(4)	119.1(3)
C(2)–B(1)–O(2)	121.5(3)	C(9)–B(6)–O(5)	121.8(3)
O(7)–B(8)–O(8)	117.2(3)	O(9)–B(7)–O(10)	116.9(3)
C(16)–B(8)–O(7)	119.4(3)	C(18)–B(7)–O(9)	118.6(3)
C(16)–B(8)–O(8)	123.6(3)	C(18)–B(7)–O(10)	124.5(3)

Acknowledgements

We acknowledge the EPSRC support of the X-ray Crystallographic Service at UWC.

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