Pergamon

PII: S0277-5387(96)00559-1

Polyhedron Vol. 16, No. 13, pp. 2325–2328, 1997

0277–5387/97 $17.00+0.00

COMMUNICATION

Isolation and structural characterization of novel compounds containing B_4O_2 rings

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(Received 31 October 1996; accepted 15 November 1996)

Abstract—Two compounds containing planar six-membered B_4O_2 rings have been synthesized and characterized by X-ray crystallography, namely $[B_4O_2(OH)_4]\cdot[NH_2Me_2][Cl]$ and $[B_4O_2(dab)_2]$ (dab = 1,4-Bu^t-1,4-diazabutadiene), the former compound providing a model for one possible structure of boron monoxide. $\{BO\}_x$. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: boron; diboron; X-ray; inorganic ring; cyclic; tetraboron.

There are many examples of cyclic compounds containing boron and various other elements [1], but six-membered B_4O_2 rings containing B—B bonds and three-coordinate boron centres have not yet been described.† Such compounds are interesting, however, in view of their relationship to possible structures of solid boron monoxide, $\{BO\}_x$, as discussed by Brotherton and coworkers [3]. Whilst a number of routes to $\{BO\}_x$ have been described, that reported by Brotherton *et al.* is derived from dehydration of dibororontetrahydroxide, $B_2(OH)_4$ (**1**), itself obtained from hydrolysis of $B_2(NMe_2)_4$ (**2**) [3,4]. In the course of studying reactions between **2** and catechols (cat), which afforded diborane(4) compounds of the type $B_2(cat)_2$ [5], we examined the reaction between **2** and tetrachlorocatechol and obtained both the anticipated compound $B_2(1,2\text{-}O_2C_6Cl_4)_2$ (**3**), as the major product,

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† We note, however, a recent report by Meller and Maringgele on the preparation of the compounds $B_4O_2(NR_2)_4$ (R = Pr^i, Bu^t) [2].

together with smaller quantities of an unexpected compound identified by X-ray crystallography as $[B_4O_2(OH)_4] \cdot [NH_2Me_2][Cl]$ (**4**).*†

Compound **4** comprises neutral, crystallographically centrosymmetric molecules of the planar six-membered ring compound $B_4O_2(OH)_4$ (Fig. 1), in which the oxygens have a 1,4 disposition in the ring and each boron is bonded to an exocyclic OH group. The B—B length [B(1)—B(2a) 1.732(3) Å] is somewhat longer than is typical for most diborane(4) compounds [7], although it is typical of the B—B distances observed in tri- and tetraboron compounds of the general formula $X\{B(NMe_2)\}_xX$ ($x = 3,4$), many of which have been characterized by Nöth and coworkers [8]. The intra-ring B—O bond lengths [av. B—O 1.382 Å) are similar to the B—O distances found in $B_2(cat)_2$ compounds [7], but the exocyclic B—OH bond lengths are a little shorter (av. 1.356 Å); none of the interbond angles associated with the B_4O_2 ring deviate substantially from 120°. In addition, crystals of **4** contain 1 equiv of cocrystallized dimethylammonium chloride, $[NH_2Me_2]Cl$,‡ the chloride ions being hydrogen bonded to one N—H proton (NH···Cl 2.309 Å) and two OH protons (OH···Cl 2.251, 2.292 Å).

The compound $B_4O_2(OH)_4$, which is most likely a hydrolysis product of **2**, presumably resulted from the presence of traces of water in incompletely dried tetrachlorocatechol,§ and may be viewed formally as a dehydration product of **1** according to eq. (1). Complete dehydration would lead to a ladder type polymer which represents one possible structural form of $\{BO\}_x$ with numerous oligomeric species with terminal hydroxides as possible intermediates. Indeed, preliminary experiments in which the hydrolysis of **2** is followed by ^{11}B-$\{^1H\}$ NMR spectroscopy indicate that several species are present in solution. We note also that Malhotra [9] has described the reaction between **2** and H_2S, which affords the related compound $B_4S_2(NMe_2)_4$ with a proposed structure analogous to that of $B_4O_2(OH)_4$.

$$2B_2(OH)_4 \rightarrow B_4O_2(OH)_4 + 2H_2O \qquad (1)$$

A second example of a compound containing a B_4O_2 ring was obtained from the reaction between $B_2(OMe)_4$ (**5**) [10] and $Li_2[dab]$ (dab = 1,4-Bu^t-1,4-diazabutadiene), carried out with a view to synthesizing the diborane(4) compound (dab)B—B(dab). A small yield of a crystalline product was obtained from this reaction, but was identified as the tricyclic species $B_4O_2(dab)_2$ (**6**) by X-ray crystallography, the results of which are shown in Fig. 2.¶‖ Compound **6** contains a central B_4O_2 ring (crystallographically centrosymmetric) analogous to **4** but with a somewhat shorter B—B bond length [1.683(3) Å] and slightly longer B—O bonds (av. 1.398 Å). A tricyclic structure results from the dab groups bridging across the B—B bonds, with B—N, N—C and C—C bond lengths of 1.429 (av.), 1.405 (av.) and 1.338(3) Å, respectively. A noteworthy feature of the structure of **6** is that it represents the first structurally characterized example of a 1,2 as opposed to a 1,1 attachment of two chelating bidentate groups across a B—B bond [7]. Both nitrogen atoms are trigonal planar (av. sum of angles 359.8°), thus implying that the lone pairs are involved in π-bonding within the ring. With this in mind, we note that **6** has a total of 16 π-

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* Compound **3** was obtained as a white powder with typical isolated yields of 50% according to the general preparative method described for $B_2(cat)_2$ compounds in [5] and was characterized by elemental analysis, high-resolution mass spectrometry (HRMS) and ^{11}B-$\{^1H\}$ NMR spectroscopy. $C_{12}B_2Cl_8O_4$ requires C, 28.1. Found C, 28.6%. HRMS: M^+ (100%) 507.755; $^{12}C_{12}{}^{10}B_2{}^{35}Cl_8{}^{16}O_4$ requires 507.756. ^{11}B-$\{^1H\}$ NMR $\delta \sim 21$. On occasions, when incompletely dried tetrachlorocatechol was used, small quantities of colourless crystals of **4** were also obtained. Difficulties in separating **4** from **3** prevented satisfactory elemental analytical data from being obtained for **4**, but a ^{11}B-$\{^1H\}$ NMR spectrum showed a resonance at δ 29 due to **4**.

† Compound **4**: $C_4H_{20}B_4Cl_2N_2O_6$, $M_r = 306.36$, triclinic, space-group $P\bar{1}$, $a = 5.4792(13)$, $b = 8.502(2)$, $c = 9.141(2)$ Å, $\alpha = 117.350(5)$, $\beta = 96.762(6)$, $\gamma = 93.075(5)°$, $U = 372.8(2)$ Å^3, $Z = 1$, $D_c = 1.365$ g cm^{-3}, $\mu = 0.449$ mm^{-1} (Mo-K_α radiation, $\lambda = 0.71073$ Å), $F(000) = 160$; wR_2 (all data) $= \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2} = 0.0871$ for 86 parameters, including anisotropic displacement parameters for non-hydrogen atoms and isotropic constrained hydrogen atoms, by refinement on F^2 from all 1604 measured unique data ($R_{int} = 0.0339$, θ_{max} 28.29°) measured at 160 K on a Siemens SMART CCD diffractometer and uncorrected for absorption; conventional $R = 0.0352$ for F values of 1305 reflections with $F^2 > 2\sigma(F^2)$ [6].

‡ The presence of dimethylammonium chloride results from the use of HCl in the preparation of $B_2(cat)_2$ compounds [5].

§ Tetrachlorocatechol was procured commercially as a hydrate and dried by azeotroping with toluene.

¶ A solution of **5** (0.32 g, 2.20 mmol) in toluene (20 cm^3) was added dropwise over a period of 2 h to a suspension of $Li_2[dab]$ [11] (0.8 g, 4.39 mmol) in toluene (30 cm^3) at −78°C. The resulting mixture was then allowed to warm to room temperature and stir overnight after which time all volatiles were removed *in vacuo* resulting in an orange–brown residue. Redissolution in thf (tetrahydofuran 5 cm^3) and cooling to −20°C afforded a small crop of colourless crystals of **6** after a few days. NMR data for **6** (C_6D_6): ^1H: δ 1.33 (Bu^t), 6.41 (=CH); ^{13}C-$\{^1H\}$: δ 114.9 (=CH), 52.3 [$C(CH_3)_3$], 32.1 [$C(CH_3)_3$]; ^{11}B-$\{^1H\}$: δ 39.3. We assume that the oxygen in **6** results from traces of water in the $Li_2[dab]$ reagent.

‖ Compound **6**: $C_{20}H_{40}B_4N_4O_2$, $M_r = 4.11.80$ monoclinic, space group $P2_1/c$, $a = 10.417(9)$, $b = 9.998(7)$, $c = 11.462(9)$ Å, $\beta = 91.78(6)°$, $U = 1193(2)$ Å^3, $Z = 2$, $D_c = 1.146$ g cm^{-3}, $\mu = 0.71$ cm^{-1} (Mo-K_α radiation, $\lambda = 0.71073$ Å), $F(000) = 448$; wR_2 (all data) = 0.0901 for 145 parameters, including anisotropic displacement parameters for non-hydrogen atoms and isotropic constrained hydrogen atoms, by refinement on F^2 from all 2732 unique data ($R_{int} = 0.0507$, θ_{max} 27.50°) measured at 178 K on a Siemens $P4$ diffractometer and uncorrected for absorption; conventional $R = 0.0604$ for F values of 2726 reflections with $F^2 > 2\sigma(F^2)$ [6].

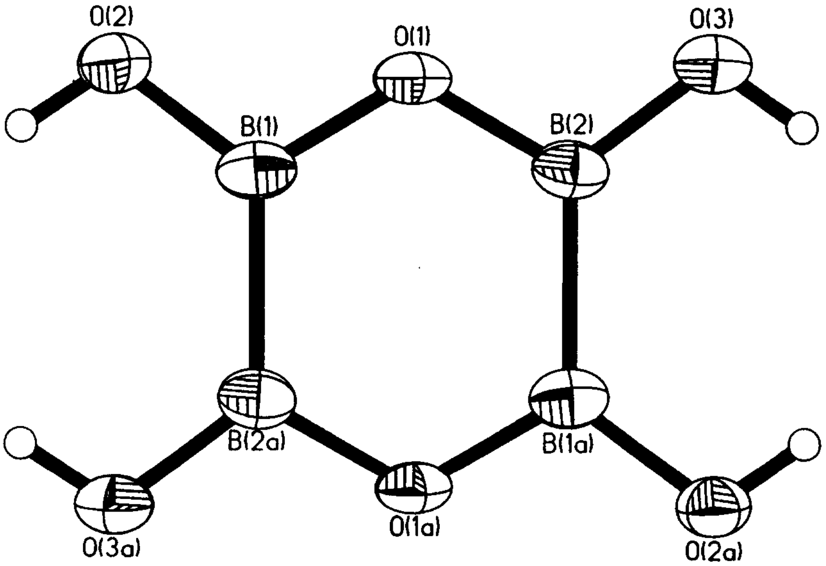

Fig. 1. A view of the molecular structure of $B_4O_2(OH)_4$ showing the atom-numbering scheme. The $[NH_2Me_2]^+$ and chloride ions are not shown. Selected bond lengths and angles include: B(1)—B(2a) 1.732(3), B(1)—O(1) 1.378(3), B(2)—O(1) 1.385(3), B(1)—O(2) 1.361(3), B(2)—O(3) 1.350(3) Å; O(1)—B(1)—O(2) 113.8(2), O(1)—B(1)—B(2a) 120.0(2), O(2)—B(1)—B(2a) 126.1(2), O(1)—B(2)—O(3) 114.4(2), O(1)—B(2)—B(1a) 119.1(2), O(3)—B(2)—B(1a) 126.4(2), B(1)—O(1)—B(2) 120.5(2)°. Symmetry transformation used to generate equivalent atoms: $-x+2$, $-y+1$, $-z+1$.

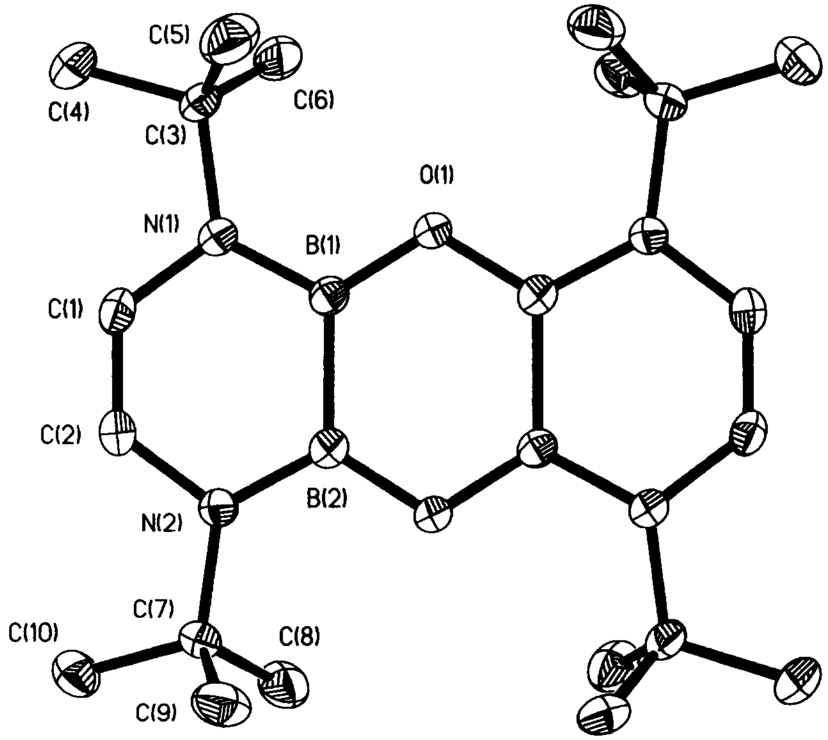

Fig. 2. A view of the molecular structure of **6** showing the atom-numbering scheme. Selected bond lengths and angles include: B(1)—B(2) 1.683(3), B(1)—O(1) 1.399(2), B(2)—O(1a) 1.397(2), B(1)—N(1) 1.430(3), B(2)—N(2) 1.428(3), N(1)—C(1) 1.405(2), N(2)—C(2) 1.405(2), C(1)—C(2) 1.338(3) Å; O(1)—B(1)—B(2) 121.5(2), O(1)—B(1)—N(1) 121.2(2), N(1)—B(1)—B(2) 117.3(2), O(1a)—B(2)—B(1) 121.0(2), O(1a)—B(2)—N(2) 121.2(2), N(2)—B(2)—B(1) 117.7(2), B(1)—O(1)—B(2a) 117.4(2), B(1)—N(1)—C(1) 116.2(2), N(1)—C(1)—C(2) 126.4(2), C(1)—C(2)—N(2) 126.2(2), C(2)—N(2)—B(2) 116.0(2)°. Symmetry transformation used to generate equivalent atoms: $-x$, $-y$, $-z+2$.

electrons (counting two from each oxygen) and is therefore isoelectronic with the anthracene dianion. However, any further description of the bonding will have to await a more detailed theoretical analysis.

Acknowledgements—We thank the EPSRC for support and for studentships (A. J. S. and F. J. L.) and T. B. M. thanks NSERC of Canada. T. B. M., N. C. N. and W. C. thank NSERC, the Royal Society (London) and the British Council for supporting this collaboration *via* a series of Bilateral Exchange Awards and travel scholarships, and N. C. N. and A. H. C. thank NATO for an International Collaborative Research Grant.

REFERENCES

1. Morris, J. H., *Comprehensive Organometallic Chemistry I*, Vol. 1, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson. Pergamon Press, Oxford, 1982, p. 311. Housecroft, C. E., *Comprehensive Organometallic Chemistry II*, Vol. 1, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson. Pergamon Press, Oxford, 1995, p. 129.
2. Meller, A. and Maringgele, W., IMEBORON Conference Anstracts, Heidelberg, 1996.
3. McCloskey, A. L., Brotherton, R. J. and Boone, J. L., *J. Am. Chem. Soc.* 1961, **83,** 4750.
4. Brotherton, R. J., McCloskey, J. L., Petterson, L. L. and Steinberg, H., *J. Am. Chem. Soc.* 1960, **82,** 6242; see also, Nöth, H. and Meister, W., *Chem. Ber.* 1961, **94,** 509.
5. Lawlor, F. J., Norman, N. C., Pickett, N. L., Robins, E. G., Nguyen, P., Lesley, G., Marder, T. B., Ashmore, J. A. and Green, J. C., *Inorg. Chem.* submitted, and refs therein.
6. Sheldrick, G. M., SHELXTL. Version 5. Siemens Analytical X-Ray Instruments Inc., Madison, WI, U.S.A., 1995.
7. Clegg, W., Elsegood, M. R. J., Lawlor, F. J., Norman, N. C., Pickett, N. L., Robins, E. G., Scott, A. J., Nguyen, P., Taylor, N. J. and Marder, T. B., *Inorg. Chem.*, submitted.
8. Linti, G., Loderer, D., Nöth, H., Polborn, K. and Rattay, W., *Chem. Ber.* 1994, **127,** 1909.
9. Malhotra, S. C., *Inorg. Chem.* 1964, **3,** 862.
10. Brotherton, R. J., McCloskey, J. L., Boone, J. L. and Manasevit, H. M., *J. Am. Chem. Soc.* 1960, **82,** 6245.
11. Hermann, W. A., *Angew. Chem. Int. Edn. Engl.* 1992, **31,** 1485.