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Tetraphenoxoborate complexes of barium: crystal structures of the metalloborates [Ba(thf)$_4${B(OPh)$_4$}$_2$] and [Ba(dme)$_2${B(OPh)$_4$}$_2$] †

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The new molecular phenoxides [BaB$_2$(OPh)$_8$(thf)$_4$] 1 and [BaB$_2$(OPh)$_8$(dme)$_2$] 2 have been synthesised from B(OPh)$_3$ and either a preformed barium phenoxide or barium metal in the presence of phenol; X-ray structure determinations reveal that the barium is eight-coordinate in both compounds and that the chelating [B(OPh)$_4$]$^-$ groups occupy *trans* positions in 1 but *cis* positions in 2.

Progress in metal alkoxide chemistry continues to be driven largely by the search for soluble and/or volatile precursors for the preparation of oxide materials from solution or from the vapour phase, and much synthetic effort has been directed at the preparation of heteronuclear alkoxides because of the potential advantages of 'single-source' precursors in mixed-oxide processing.[1] We have been interested in preparing single-source precursors to the non-linear optical material β-barium borate, β-BaB$_2$O$_4$ (BBO) and, while recent publications have described the sol–gel[2] and CVD[3] growth of oriented β-barium borate thin films from solutions containing mixtures of boron alkoxides and barium alkoxide or β-diketonate derivatives, alkoxides containing both barium and boron have previously not been isolated and characterised. We report here the first examples of structurally characterised Group 2 metalloborates [BaB$_2$(OPh)$_8$(thf)$_4$] **1** and [BaB$_2$(OPh)$_8$(dme)$_2$] **2**.

The direct approach to heteronuclear alkoxide synthesis, *i.e.* the reaction between constituent alkoxides, relies upon the Lewis acidity of at least one of the elements involved to induce the formation of alkoxide bridges between the different elements. However, the Lewis acidity of boron in the alkoxides B(OR)$_3$ is lowered by oxygen to boron π-donation and the only structurally characterised examples of tetrahedral boron alkoxide species contain strongly basic methoxide ligands, *e.g.* [(MeOH)$_2$LiB(OMe)$_4$],[4] (PhCH$_2$NMe$_3$)[B(OMe)$_4$],[5] and polymeric [La{B(OMe)$_4$}(NO$_3$)$_2$(MeOH)$_2$]$_n$.[6] Boron aryloxides B(OAr)$_3$, on the other hand, have been shown to be more Lewis acidic and form adducts with nitrogen bases.[7] Given the ill-defined nature of "Ba(OMe)$_2$" and the tendency of methoxides in general to be more highly associated and thereby less soluble,[8] we selected a 1:2 mixed Ba–B aryloxide containing [B(OAr)$_4$]$^-$ groups as a synthetic target for a single-source BBO precursor.

Hexanuclear [Ba$_6$(OPh)$_{12}$(tmeda)$_4$] was initially chosen as a soluble source of "Ba(OPh)$_2$",[9] and colourless crystalline solvates **1**·2thf or **2**·0.5dme were obtained from reactions with B(OPh)$_3$ in the appropriate ether solvent. A more convenient route to **1** and **2** is the direct reaction between barium metal, B(OPh)$_3$ and phenol in thf or dme respectively.‡

The structures of **1** and **2**§ are shown in Figs. 1 and 2 respectively. In both compounds the barium is eight-coordinate and phenoxo groups bridge between barium and boron, such that the tetrahedral [B(OPh)$_4$]$^-$ groups thus formed can be regarded as chelating ligands.

Interestingly, the arrangement of the phenoxoborate and ether ligands is markedly different in the two compounds. The barium in **1** lies on a crystallographic inversion centre, with four thf ligands occupying an equatorial belt and two bidentate

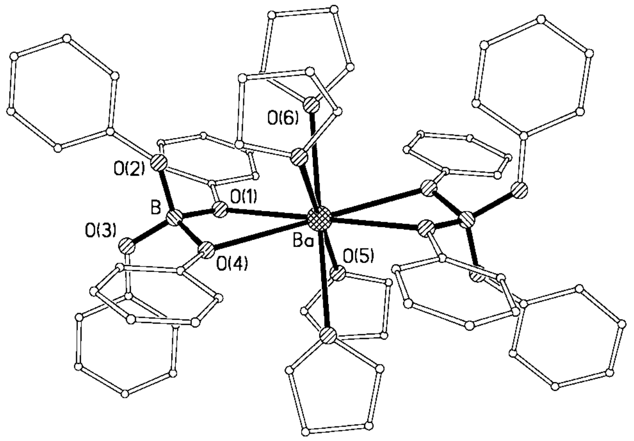

Fig. 1 The molecular structure of [BaB$_2$(OPh)$_8$(thf)$_4$] **1** without H atoms and thf disorder. Selected bond distances (Å) and angles (°): Ba–O(1) 2.8086(13), Ba–O(4) 2.8479(13), Ba–O(5) 2.8131(16), Ba–O(6) 2.8027(15), B–O(1) 1.492(2), B–O(4) 1.497(2), B–O(2) 1.453(3), B–O(3) 1.447(2); O(1)–Ba–O(4) 47.32(4), O(5)–Ba–O(6) 108.09(5), O(1)–B–O(4) 98.80(14), O(2)–B–O(3) 111.32(11), Ba–O(1)–B 104.79(10), Ba–O(4)–B 102.89(10).

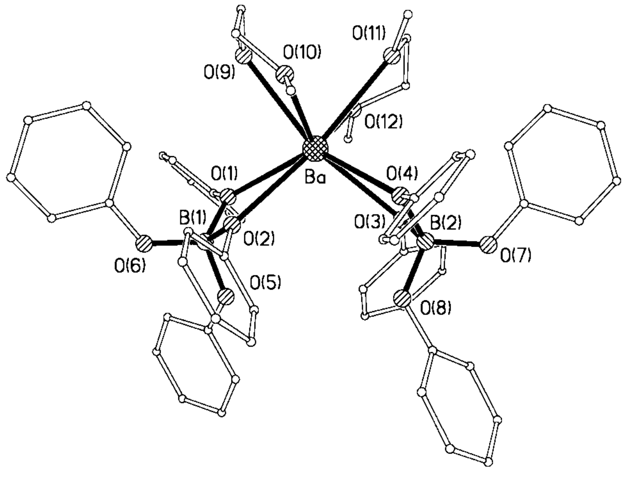

Fig. 2 The molecular structure of [BaB$_2$(OPh)$_8$(dme)$_2$] **2** without H atoms. Selected bond distances (Å) and angles (°): Ba–O(1) 2.794(2), Ba–O(2) 2.721(2), Ba–O(3) 2.698(2), Ba–O(4) 2.762(2), Ba–O(9) 2.780(2), Ba–O(10) 2.800(2), Ba–O(11) 2.808(2), Ba–O(12) 2.826(2), B(1)–O(1) 1.490(4), B(1)–O(2) 1.488(4), B(2)–O(3) 1.486(4), B(2)–O(4) 1.495(4), B(1)–O(5) 1.453(4), B(1)–O(6) 1.459(4), B(2)–O(7) 1.450(4), B(2)–O(8) 1.449(4); O(1)–Ba–O(2) 48.39(6), O(3)–Ba–O(4) 49.00(6), O(9)–Ba–O(10) 59.26(7), O(11)–Ba–O(12) 59.31(7), O(1)–B(1)–O(2) 98.8(2), O(3)–B(2)–O(4) 98.9(2), O(5)–B(1)–O(6) 108.7(3), O(7)–B(2)–O(8) 108.5(3), Ba–O(1)–B(1) 103.5(18), Ba–O(2)–B(1) 106.86(18), Ba–O(3)–B(2) 105.75(17), Ba–O(4)–B(2) 102.61(18).

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3533/

$[B(OPh)_4]^-$ anions in *trans*-axial positions such that the plane defined by the four thf oxygens is perpendicular to that defined by the four oxygens of the bridging phenoxides. In contrast, the mutually *cis* arrangement of the phenoxoborate ligands in **2** must be a result of reduced steric requirements of the mutually *cis* dme ligands as compared with the four thf ligands in **1**, an arrangement which allows the phenoxoborate ligands to bind more tightly in **2** than in **1**. Compared with the average bite angle of 59.3° for the dme ligands, the smallest angle between pairs of thf ligands is 71.8°. The dihedral angle between planes defined by Ba, O(9) and O(10) and Ba, O(11) and O(12) is 77.1°.

Bonds between Ba and OPh ligands [2.8086(13), 2.8479(13) Å for **1** and 2.698(2)–2.794(2) for **2**] are longer than those for terminal and μ-aryloxides in previously reported homonuclear barium compounds where the coordination number of Ba (5, 6 or 7) is lower than that for **1** and **2**.[9,10] The $Ba–O_{thf}$ and $Ba–O_{dme}$ bonds differ little from those in other ether complexes of barium.[10,11] The boron atoms adopt a distorted tetrahedral coordination geometry, as has also been observed in the structurally characterised compounds containing the $[B(OMe)_4]^-$ anion. The chelating O–B–O angles in the $[B(OPh)_4]^-$ ligands [98.80(14)° in **1** and 98.8(2), 98.9(2)° in **2**] are significantly reduced from the tetrahedral value, and are similar to that for the bridging $[B(OMe)_4]^-$ groups in $[La\{B(OMe)_4\}(NO_3)_2(MeOH)_2]_n$ [98.5(3)°][6] but smaller than the reduced dihedral angles in isolated, tetragonally elongated $[B(OMe)_4]^-$ anions [103.0(2) and 101.2(2)°].[5] The angles subtended at Ba by the $[B(OPh)_4]^-$ ligands are 47.32(4)° in **1** and 48.39(6), 49.00(6)° in **2**, slightly larger than that subtended by the chelating carboxylate ligands in $[Ba(O_2CCH_3)_2(18\text{-crown-}6)]$ [45.0(1)°], where the oxygen donor atoms of the crown ether occupy the equatorial plane in a similar fashion to the thf ligands in **1**.[11]

1 and **2** are soluble in their parent ethers and in hot toluene. ^1H and ^{13}C NMR solution spectra contain only one set of phenoxide resonances, indicating that the bridging and terminal phenoxide groups undergo site exchange readily *via* a dynamic process, in common with many alkoxide compounds.

In conclusion, we have shown that $[B(OPh)_4]^-$ can act as a chelating ligand towards barium and that the nature of the compounds formed depends on the complementary ligands on barium. To investigate the scope of $[B(OPh)_4]^-$ as a ligand, we have now synthesised a range of Group 2 metalloborates and it is interesting to note that our attempts to prepare analogues of **1** and **2** with polydentate ether ligands resulted in compounds containing discrete $[BaL_n]^{2+}$ cations and $[B(OPh)_4]^-$ anions.[12] The structures of these compounds and results from thin-film deposition and materials studies will be described elsewhere.

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Notes and references

‡ Preparation of **1**. Method (A). A solution of $[Ba_6(OPh)_{12}(tmeda)_4]$ (0.5 g, 0.23 mmol) in thf (15 cm^3) was added to $B(OPh)_3$ (0.79 g, 2.72 mmol) to give a clear solution. The solid obtained by reducing the volume of the solution under reduced pressure was filtered off and recrystallised from thf (10 cm^3) to give colourless crystals of **1**·2thf (0.21 g). A further crop (0.16 g) was obtained from the mother liquor. Method (B). A mixture of metallic barium (0.79 g, 5.73 mmol), $B(OPh)_3$ (3.36 g, 11.58 mmol) and PhOH (1.09 g, 11.58 mmol) in thf (30 cm^3) was stirred at room temperature overnight. The resultant turbid grey solution was filtered and the filtrate reduced to half volume under reduced pressure. Cooling to −30 °C produced well formed crystals of **1**·2thf (5.26 g, 77%). Microanalysis for **1**: C, 63.9; H, 6.1%. $C_{64}H_{72}BaB_2O_{12}$ requires C, 64.48; H, 6.09%. Spectroscopic data for **1**: ^1H NMR (200 MHz, C_4D_8O): δ_H 7.08 (m, 32H, *o*- and *m*-C_6H_5), 6.82 (m, 8H, *p*-C_6H_5), 3.71 [br m, 16H, OCH_2 (thf)], 1.87 [br m, 16H, OCH_2CH_2 (thf)]. ^{13}C NMR (50.3 MHz, C_4D_8O): δ_C 158.8 (*ipso*-C_6H_5), 130.8 (*o*-C_6H_5), 122.5 (*m*-C_6H_5), 122.0 (*p*-C_6H_5), 69.6 [OCH_2 (thf)], 27.8 [OCH_2CH_2 (thf)]. ^{11}B NMR (96.3 MHz, thf, $BF_3\cdot Et_2O$ reference): δ_B 1.93 (s, $w_{1/2} = 27$ Hz). IR (Nujol mull on CsI plates): 1595 (s), 1540 (w), 1487 (m), 1257 (m), 1228 (s, br), 1166 (w), 1151 (w), 1070 (m), 1051 (m), 1025 (m), 1000 (m), 917 (m, br), 890 (m, br), 856 (w), 811 (w), 752 (s), 690 (s), 507 (m) cm^{-1}.

Preparation of **2**. Method (A). A solution of $[Ba_6(OPh)_{12}(tmeda)_4]$ (0.69 g, 0.29 mmol) and $B(OPh)_3$ (1.00 g, 3.45 mmol) in dimethoxyethane (20 cm^3) was stirred at room temperature overnight. Filtration and removal of all volatiles under vacuum gave a colourless, crystalline solid. Recrystallisation from hot toluene (10 ml) gave colourless crystals of **2**·0.5dme (1.50 g, 80%). Method (B). A mixture of metallic barium (0.81 g, 5.89 mmol), $B(OPh)_3$ (3.49 g, 12.01 mmol) and PhOH (1.13 g, 12.01 mmol) was stirred in dimethoxyethane (30 cm^3) at room temperature overnight. The resultant grey solution was filtered and volatiles were removed under vacuum to give a colourless, oily solid. Recrystallisation from hot toluene (20 ml produced large crystals of **2**·0.5dme (4.40 g, 69%). Microanalysis for **2**: C, 62.4; H, 5.4%. $C_{56}H_{60}BaB_2O_{12}$ requires C, 62.1; H, 5.6%. Spectroscopic data for **2**: ^1H NMR (200 MHz, C_4D_8O): δ_H 7.08 (m, 32H, *o*- and *m*-C_6H_5), 6.82 (m, 8H, *p*-C_6H_5), 3.71 [br m, 16H, OCH_2 (thf)], 1.87 [br m, 16H, OCH_2CH_2 (thf)]. ^{13}C NMR (50.3 MHz, C_4D_8O): δ_C 158.9 (*ipso*-C_6H_5), 130.8 (*o*-C_6H_5), 122.5 (*m*-C_6H_5), 122.0 (*p*-C_6H_5), 69.6 [OCH_2 (thf)], 27.8 [OCH_2CH_2 (thf)]. ^{11}B NMR (96.3 MHz, thf, $BF_3\cdot Et_2O$ reference): δ_B 1.93 (s, $w_{1/2} = 27$ Hz). IR (Nujol mull on CsI plates): 1594 (s), 1537 (w), 1496 (vs), 1325 (m), 1298 (m), 1286 (m), 1242 (s, br), 1232 (s, br), 1190 (m), 1168 (m), 1151 (m), 1132 (w), 1110 (m), 1068 (m, br), 1024 (m, br), 917 (m), 887 (m), 854 (m), 829 (m), 789 (w), 752 (s), 736 (m), 692 (s), 667 (w), 634 (w), 593 (m), 576 (w), 532 (w), 518 (m), 430 (w) cm^{-1}.

§ Crystallographic data for **1**·2thf: $C_{64}H_{72}B_2BaO_{12}\cdot 2C_4H_8O$, $M = 1336.4$, triclinic, $P\bar{1}$, $a = 11.0751(9)$, $b = 11.7693(10)$, $c = 13.5004(11)$ Å, $\alpha = 104.461(2)$, $\beta = 104.083$, $\gamma = 93.135(2)°$, $V = 1640.2(2)$ Å^3, $Z = 1$, $T = 160$ K. The structure was determined[13] from 7185 unique absorption-corrected reflections (10382 measured, $\theta < 28.42°$, $R_{int} = 0.0227$); $wR2 = 0.0749$ for all F^2 values, conventional $R = 0.0279$. Two-fold disorder was resolved for one or two C atoms of each thf, including the coordinated molecules.

Crystallographic data for **2**·0.5dme: $C_{56}H_{60}B_2BaO_{12}\cdot 0.5C_4H_{10}O_2$, $M = 1129.1$, monoclinic, $P2_1/n$, $a = 11.2348(6)$, $b = 20.0431(11)$, $c = 25.0246(13)$ Å, $\beta = 90.881(2)°$, $V = 5634.4(5)$ Å^3, $Z = 4$, $T = 160$ K. The structure was determined[13] from 13367 unique absorption-corrected reflections (35012 measured, $\theta < 28.88°$, $R_{int} = 0.0539$); $wR2 = 0.0985$ for all F^2 values, conventional $R = 0.0443$. CCDC reference 186/1652. See http://www.rsc.org/suppdata/dt/1999/3533/ for crystallographic files in .cif format.

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