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# Synthesis and structural characterization of some novel metalloboroxides bearing boron-bound mesityl and fluoromesityl substituents: the molecular structure of the first metallaboroxane complex

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**Abstract**—Treatment of the new boronous acid HOB(fmes)$_2$ (**1**) (fmes = 2,4,6-$(CF_3)_3C_6H_2$) with *n*-butyllithium in diethyl ether/pentane affords after work-up the dimer [Li(thf)OB(fmes)$_2$]$_2$ (**2**). Reaction of $[Mo_2(NMe_2)_6]$ with two equivalents of **1** in toluene gives the amido-boroxide complex $Mo_2(NMe_2)_4$[OB(fmes)$_2$]$_2$ (**3**). Treatment of $CuBr_2$ with LiOB(Mes)$_2$ (mes = 2,4,6-$Me_3C_6H_2$) in tetrahydrofuran affords after work-up and addition of excess pyridine the monomeric copper(II) boroxide {Cu[$O_3B_2$(mes)$_2$]$_2$[Li($CH_3CN$)($C_5H_5N$)]$_2$} (**4**), containing the new ligand mesB(O)OB(O)mes, as a result of loss of mesitylene and formation of a B—O—B bond. **2** and **4** have been structurally characterized. © 1997 Elsevier Science Ltd

*Keywords*: boron; molybdenum; copper; mesityl; boroxide; fluorine.

As part of an interest [1] in developing the chemistry of ligands containing the bulky, highly electron-withdrawing substituent, 2,4,6-$(CF_3)_3C_6H_2$(fmes), we describe here the synthesis and characterization of the new boronous acid HOB(fmes)$_2$ (**1**) and the first metal complexes containing the OB(fmes)$_2$ ligand. As a ligand, the —OB(fmes)$_2$ group may be regarded as a highly electron-withdrawing quasi-alkoxide, the incipient acidity of the boron centre being further enhanced by the strong electron-withdrawing capacity of the fmes substituents. We also describe the first example of a metallaboroxane [2], arising from treatment of $CuBr_2$ with LiOB(mes)$_2$.

## RESULTS AND DISCUSSION

### *Fluoromesityl derivatives*

The reaction of fmesLi (2 equivalents) with $BCl_3$ in diethyl ether/pentane (−78°C) gives multigram quantities of (fmes)$_2$BCl. Attempts to prepare B(fmes)$_3$ by treatment of $BCl_3$ with three equivalents of fmesLi also gave the di-substituted species presumably a consequence of the severe steric hindrance of the boron centre by the two fluoromes substituents. However, hydrolysis of (fmes)$_2$BCl readily gives the boronous acid (fmes)$_2$BOH (**1**). Treatment of **1** with nBuLi in diethyl ether (−20°C), followed by recrystallization from thf/pentane/ether affords colourless crystals of the lithium salt [(thf)LiOB(fmes)$_2$]$_2$ (**2**) in high yield. The structure of **2** is shown in Fig. 1. Selected bond lengths and angles are collected in Table 1. The general features of **2** are similar to those reported [3] for the dimeric complex [Li(thf)(OBmes)$_2$]$_2$, with approximate trigonal planar boron atoms and a crystallographically imposed 2-fold rotation axis through the lithium atoms, but with some variations in the bonding parameters due to the differing steric and electronic properties of the two ligand sets. The shorter B—O bonds are found in **2** (1.298(3) vs 1.317(6) Å in the OB(mes)$_2$ derivative), whilst the Li—O bonds are somewhat longer (1.883(5), 1.874(5) Å in **2** *cf* 1.853(7), 1.845(7) Å). This is consistent with greater

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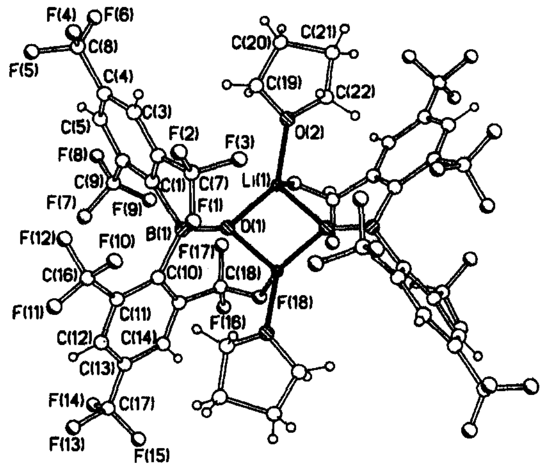

Fig. 1. Molecular structure of **2**, with most non-hydrogen atoms labelled. Only one component of each disordered group is shown.

localization of electron density between B and O at the expense of the Li—O interaction. The C(1)—B(1)—C(10) angle in **2** has opened up to 123.8(2)° (*cf* 120.9(4)° in its *per protio* analogue) which is most likely a consequence of the increased size of the $CF_3$ substituents in **2** but which may also in-part be due to weak Li···F interactions (e.g. Li(1)···F(18a) = 2.231(6) Å).

The boronous acid **1** reacts slowly (2 days) with $Mo_2(NMe_2)_6$ to give yellow crystalline $Mo_2(NMe_2)_4[OB(fmes)_2]_2$ (**3**). In solution, **3** is presumed to exist as the gauche rotamer by comparison of its NMR data with those of its *per-protio* mesityl tungsten analogue [4] which has also been structurally characterised: in toluene-$d_8$ at −60°C two sets of signals are observed in a 1 : 1 ratio attributable to the proximal and distal $NMe_2$ groups. At *ca* 10°C one of the sets of $NMe_2$ groups is broadened and is lost to the baseline at *ca* 50°C. The other $NMe_2$ group remains sharp until *ca* 70°C. Unfortunately, crystals suitable for X-ray study could not be obtained due to persistent twinning.

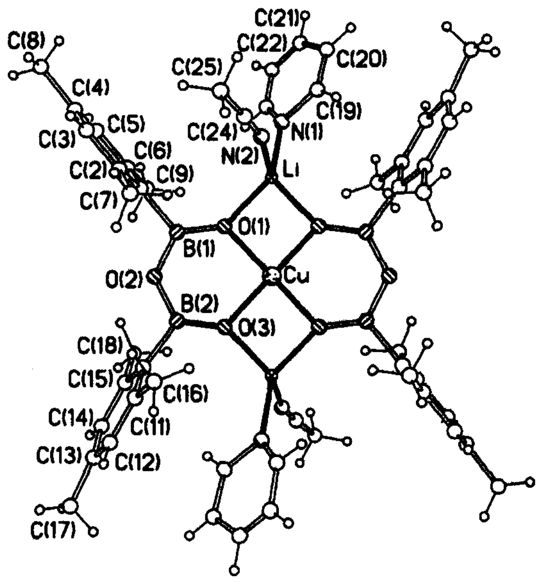

Fig. 2. Molecular structure of **4**, with most non-hydrogen atoms labelled.

### *A metallaboroxane complex*

Interaction of the lithium salt $LiOB(mes)_2$ (2 equivalents) with $CuBr_2$ in tetrahydrofuran, followed by the addition of excess pyridine and recrystallization from acetonitrile gave relatively air-stable purple prisms of the paramagnetic complex $\{Cu[O_3B_2(mes)_2]_2[Li(CH_3CN)(C_5H_5N)]_2\}$ (**4**) in low yield (*ca* 17%). The EPR spectrum of **4** in $CH_2Cl_2$ at room temperature is typical of square-planar copper(II) [5(a)-(c)]: four fairly well-resolved peaks are observed with $g_1 = 2.05$, $g_2 = 2.10$, $g_3 = 2.16$ and $g_4 = 2.21$. The $M[O_3B_2(mes)_2]$ fragment may be regarded as a metallaboroxane an example of which, to our knowledge, has not previously been observed. A view of the complex is shown in Fig. 2. Selected bond lengths and angles are collected in Table 2.

The OBOBO rings are planar, consistent with delocalised $\pi$-bonding between the oxygen and boron

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

| | | | |
|---|---|---|---|
| B(1)—O(1) | 1.298(3) | B(1)—C(1) | 1.626(4) |
| B(1)—C(10) | 1.634(4) | Li(1)—O(1) | 1.883(5) |
| Li(1)—O(1a) | 1.874(5) | Li(1)—O(2) | 1.919(6) |
| Li(1)—F(18a) | 2.231(6) | | |
| O(1)—B(1)—C(1) | 117.5(2) | O(1)—B(1)—C(10) | 118.7(2) |
| C(1)—B(1)—C(10) | 123.8(2) | B(1)—O(1)—Li(1a) | 137.0(2) |
| B(1)—O(1)—Li(1) | 139.5(2) | Li(1a)—O(1)—Li(1) | 83.5(2) |
| O(1a)—Li(1)—O(1) | 96.5(2) | O(1a)—Li(1)—O(2) | 121.8(3) |
| O(1)—Li(1)—O(2) | 138.7(3) | O(1a)—Li(1)—F(18a) | 87.8(2) |
| O(1)—Li(1)—F(18a) | 107.9(3) | O(2)—Li(1)—F(18a) | 89.8(2) |

Symmetry transformations used to generate equivalent atoms: a: $-x+1, y, -z+3/2$.

Table 2. Selected bond lengths (Å) and angles (°) for **4**

| | | | |
|---|---|---|---|
| Cu—O(3) | 1.917(2) | Cu—O(1) | 1.928(2) |
| O(1)—B(1) | 1.322(4) | O(1)—Li | 1.907(5) |
| O(3)—B(2) | 1.319(4) | B(1)—O(2) | 1.393(4) |
| B(1)—C(1) | 1.592(4) | O(2)—B(2) | 1.396(4) |
| B(2)—C(10) | 1.594(4) | Li—O(3a) | 1.887(5) |
| Li—N(1) | 2.063(6) | Li—N(2) | 2.098(6) |

| | | | |
|---|---|---|---|
| O(3)—Cu—O(1) | 94.36(8) | O(3a)—Cu—O(1) | 85.64(8) |
| B(1)—O(1)—Li | 140.3(2) | B(1)—O(1)—Cu | 124.9(2) |
| Li—O(1)—Cu | 92.8(2) | B(2)—O(3)—Li(a) | 140.3(2) |
| B(2)—O(3)—Cu | 125.9(2) | Li(a)—O(3)—Cu | 93.8(2) |
| O(1)—B(1)—O(2) | 124.5(3) | O(1)—B(1)—C(1) | 121.3(3) |
| O(2)—B(1)—C(1) | 114.2(3) | B(1)—O(2)—B(2) | 126.1(3) |
| O(3)—B(2)—O(2) | 123.9(3) | O(3)—B(2)—C(10) | 119.2(3) |
| O(2)—B(2)—C(10) | 116.9(3) | O(3a)—Li—O(1) | 87.1(2) |
| O(3a)—Li—N(1) | 118.2(3) | O(1)—Li—N(1) | 128.1(3) |
| O(3a)—Li—N(2) | 118.3(3) | O(1)—Li—N(2) | 109.2(3) |
| N(1)—Li—N(2) | 97.7(2) | | |

Symmetry transformations used to generate equivalent atoms: a: $-x$, $-y$, $-z$.

atoms, and they chelate to the copper centre in a symmetrical fashion, enforcing approximate square planar geometry at the metal centre with angles of 85.64(8) and 94.36(8)°. The B—O bonds B(1)—O(1) and B(2)—O(3), *viz* 1.322(2) and 1.319(4) Å respectively, are indicative of some $\pi$ interaction which could weaken the Cu—O bonds (1.917(2) and 1.928(2) Å). The other main distortion arises from the restricted bite of the boroxide ligands which spans two triply bridging oxo groups with a B—O—B angle of 126.1(3)°. The resulting coordination geometry at each boron is now pseudo trigonal planar with angles in the range 114.2(3) to 124.5(3)°. The lithium groups bridge opposite edges and are retained within the equatorial plane, so the molecule has a pseudo-two-fold axis of symmetry passing through O(2), Cu and O(2a); the exact crystallographic symmetry is *Ci*. Lithium is further coordinated by one molecule each of pyridine and acetonitrile, to give a distorted tetrahedral geometry.

## EXPERIMENTAL

### *General*

All manipulations were carried out under nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry at the University of Durham and at Imperial College. NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400.0 MHz ($^1$H), and 376.3 MHz ($^{19}$F) or on a JEOL FX90Q ($^{19}$F); chemical shifts are referenced to the residual *protio* impurity of the deuterated solvent; ESR on a Varian E-12 (X-band); IR spectra (Nujol mulls, CsI windows), Perkin-Elmer 577 and 457 grating spectrophotomers. The ligand fmes was prepared by a previously published procedure [6] $Mo_2(NMe_2)_6$ and $(mes)_2BOH$ were synthesised *via* the procedure described by Chisholm and co-workers [7,4]. All other chemicals were obtained commercially and used as received unless stated otherwise.

### *Preparation of* $(2,4,6\text{-}(CF_3)_3C_6H_2)_2BOH$ (**1**)

A pre-cooled solution of $BCl_3$ (8.8 cm$^3$, 8.8 mmol, 1 M in hexane) was added to a stirred solution of fmesLi (26.6 mmol) in $Et_2O$ (50 cm$^3$) at −78°C. The reaction mixture was then stirred at room temperature for 2 h to afford a colourless solution and a white precipitate. The solution was filtered from the solid which was then washed with diethyl ether (1 × 50 cm$^3$). The solvent was then removed from the combined washings under reduced pressure until *ca* 30 cm$^3$ remained. Cooling to −78°C afforded sublimable white $(fmes)_2BCl$[8] (Yield 3.2 g, 60%). Found: C, 35.8; H, 0.3. Calc. for $C_{18}H_4BClF_{18}$: C, 35.5; H, 0.7%. $^{19}$F NMR ($CDCl_3$, 90 MHz, 25°C) $\delta$: −57.0 (s, 6F, o-$CF_3$), −57.2 (s, 6F, o-$CF_3$), −63.8 (s, 6F, p-$CF_3$). Excess degassed $H_2O$ (*ca* 10 cm$^3$) was added to a stirred solution of $(fmes)_2BCl$ (3.2 g, 5.2 mmol) in $Et_2O$ (40 cm$^3$). After *ca* 30 min the ethereal layer was removed, the aqueous layer was washed twice with $Et_2O$ (2 × 25 cm$^3$) and the combined washings were dried ($MgSO_4$). Removal of volatiles *in vacuo* afforded sublimable white $(fmes)_2BOH$ (**1**) (3.1 g, yield 98%). Found: C, 37.0; H, 1.5. Calc. for $C_{18}H_5BOF_{18}$: C, 36.6; H, 0.9%: IR: 3633s ($\nu$OH), 3115w, 2359w, 1850w, 1634w, 1583m, 1418s, 1280bs, 1190bs, 1132bs, 1034s, 919s, 886s, 863m, 842s, 802m, 774m, 737w, 706s, 687s, 665s, 643s, 606w, 568w. $^{19}$F NMR ($CDCl_3$, 90 MHz, 25°C): −56.2 (s, 12F, equivalent o-$CF_3$), −63.8 (s, 6F, p-$CF_3$).

### *Preparation of* $\{Li(thf)[OB(fmes)_2]\}_2$ (**2**)

To $(fmes)_2BOH$ (2.1 g, 3.46 mmol) in $Et_2O$ (30 $cm^3$) at 0°C was added *n*BuLi (2.6 $cm^3$, 1.3 M, 3.38 mmol) dropwise. After stirring at room temperature for 5 min, thf (5 $cm^3$) and pentane (5 $cm^3$) were added. Cooling to −20°C afforded white prisms of **2** (yield 1.5 g, 80%). Found: C, 39.7; H, 2.0. Calc. for $C_{44}H_{24}B_2O_4F_{36}Li_2$: C, 39.6; H, 1.8%. $^1H$ NMR ($C_6D_6$, 25°C): 8.0 (s, 8H, m-aryl H), 2.7 (m, 8H, thf), 0.8 (m, 8H, thf). $^{19}F$ ($C_6D_6$, 25°C): −56.4 (s, 24F, o-$CF_3$), −63.1 (s, 12F, p-$CF_3$).

### *Preparation of* $\{Mo_2(NMe_2)_4[OB(fmes)_2]_2\}$ (**3**)

To $Mo_2(NMe_2)_6$ (0.67 g, 1.47 mmol) in toluene (*ca* 20 $cm^3$) was added $(fmes)_2BOH$ (1.79 g, 2.95 mmol) in toluene (*ca* 10 $cm^3$). After stirring for 2 days, volatiles were removed under reduced pressure. Extraction of the residue with pentane (30 $cm^3$) afforded a yellow solution which was concentrated and cooled to −30°C to give yellow needles of **3**. (Yield 1.24 g, 62%). Found: C, 34.2; H, 2.1; N, 3.6. Calc. for $C_{44}H_{32}N_4B_2O_2F_{36}Mo_2$: C, 34.2; H, 2.1; N, 3.6%. $^1H$ NMR ($C_6D_5CD_3$, 25°C): 7.97–8.05 (m, 8H, m-aryl H), 4.17 (bs, 6H, $NMe_2$-distal), 3.85 (s, 6H, $NMe_2$-distal), 2.18 (s, 6H, $NMe_2$-proximal), 1.6 (s, 6H, $NMe_2$-proximal).

### *Preparation of* $Cu[(mesB(O)OB(O)mes)Li(py)(CH_3CN)]_2$ (**4**)

To $CuBr_2$ (0.5 g, 2.24 mmol) in thf (*ca* 40 $cm^3$) at −78°C was added $LiOBmes_2$ (1.22 g, 4.48 mmol). The deep yellow-green solution was stirred for 12 h at room temperature. The volatile components were then removed under reduced pressure. Pentane (*ca* 40 $cm^3$) and excess pyridine (*ca* 1.8 $cm^3$) were added and the apple-green mixture stirred for 2–3 h. Removal of the solvent under reduced pressure, followed by extraction into hot MeCN (*ca* 30 $cm^3$) afforded large purple prisms of **4** on prolonged standing at room temperature. Yield 0.35 g, 17%. Found: C, 65.0; H, 6.5; N, 6.3. Calc. for $H_{60}C_{50}N_4O_6Li_2B_4Cu$: C, 64.3; H, 6.5; N, 6.0%. IR: 2301w, 2269w, 1608m, 1595m, 1559w, 1377s, 1261s, 1237s, 1165s, 1083s, 1034s, 848m, 801s, 752w, 714m, 703m, 623w, 606w, 576w, 554w, 494w, 466w, 422w. EPR ($CH_2Cl_2$, 25°C): $g_1 = 2.05$, $g_2 = 2.10$, $g_3 = 2.16$, $g_4 = 2.21$.

Table 3. Crystallographic data

| Compound | 2 | 4 |
|---|---|---|
| Formula | $C_{44}H_{24}B_2F_{36}Li_2O_4$ | $C_{50}H_{60}B_4CuLi_2N_4O_6$ |
| M | 1336.1 | 933.7 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | *C*2/*c* | *P*2$_1$/*n* |
| *a* (Å) | 23.151(2) | 12.526(2) |
| *b* (Å) | 15.1084(11) | 15.763(2) |
| *c* (Å) | 15.0452(11) | 13.157(2) |
| $\beta$ (°) | 95.780(2) | 95.84(2) |
| *V* (Å$^3$) | 5235.7(7) | 2584.2(5) |
| *Z* | 4 | 2 |
| $D_c$ (g cm$^{-3}$) | 1.695 | 1.200 |
| Radiation, $\lambda$ (Å) | Mo-$K_\alpha$ 0.71073 | Cu-$K_\alpha$, 1.54184 |
| $\mu$ (mm$^{-1}$) | 0.19 | 0.98 |
| *F*(000) | 2640 | 982 |
| Temperature (K) | 200 | 160 |
| Crystal size (mm) | 0.44 × 0.40 × 0.38 | 0.51 × 0.35 × 0.29 |
| $\theta_{max}$ (°) | 25.7 | 60.0 |
| Maximum indices *hkl* | 27, 18, 18 | 14, 17, 14 |
| Reflections measured | 11377 | 4397 |
| Unique reflections | 4510 | 3830 |
| $R_{int}$ | 0.0346 | 0.0240 |
| Transmission | 0.892–0.976 | 0.642–0.896 |
| Weighting parameters *a*, *b* | 0.0597, 5.6677 | 0.0929, 2.7309 |
| No. of refined parameters | 510 | 310 |
| *wR*2 (all data) | 0.1506 | 0.1692 |
| *R*1 ("observed" data) | 0.0519(3482) | 0.0521(3277) |
| Goodness offit | 1.082 | 1.063 |
| Max., min. el. density (e Å$^{-3}$) | 0.362, −0.252 | 0.416, −0.473 |

## *X-ray crystallography*

Crystal data for **2** and **4** are shown in Table 3, together with information on data collection and structure determination procedures. Measurements for **2** were made on a Siemens SMART CCD diffractometer. Cell parameters were refined from the observed $\omega$ angles of 6278 reflections selected from the complete data set, which was recorded with frames of 0.3° in $\omega$. Semi-empirical absorption corrections were based on equivalent and repeated reflections in the data set [9]. Measurements for **4** were made on a Stoe-Siemens four-circle diffractometer. Cell parameters were refined from $2\theta$ values of 38 reflections (50–53°) measured at $\pm\omega$ to minimise systematic errors. Intensities were measured with $\omega/\theta$ scans. Semi-empirical absorption corrections were based on sets of equivalent reflections measured at a range of azimuthal angles [9]. A correction was also made for an observed 1.5% decay in the intensities of standard reflections monitored at regular intervals.

The structures were solved by direct (**2**) and heavy-atom (**4**) methods, and refined by full-matrix least squares on $F^2$, with weighting $w^{-1} = \sigma^2(F_o^2)+(aP)^2+(bP)$, where $P = (F_o^2+2F_c^2)/3$ [8]. An isotopic extinction coefficient $x$ was refined, whereby $F_c$ is multiplied by $(1+0.001xF_c^2\lambda^3/\sin 2\theta)^{-1/4}$. Anisotropic displacement parameters were refined for all non-hydrogen atoms, while hydrogen atoms were included with a riding model for their positions and isotopic displacement parameters. Two-fold torsional disorder was resolved for several $CF_3$ groups of **2** and for the *para*-methyl groups of **4**, with restraints on geometry and displacement parameters. The residuals are defined as $wR2 = \{[w(F_o^2+2F_c^2)]/[w(F_o^2)^2]\}^{1/2}$ for all data, conventional $R1 = \|F_o|-|F_c\|/|F_o|$ for reflections having $F_o^2 > 2\sigma(F_o^2)$; the goodness of fit is calculated on $F^2$ for all data. Programs: standard Siemens SMART and Stoe D1F4 control software, Siemens SAINT area-detector frame integration, SHELXTL [9], and local programs.

Complete bond lengths and angles, H atom coordinates, and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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