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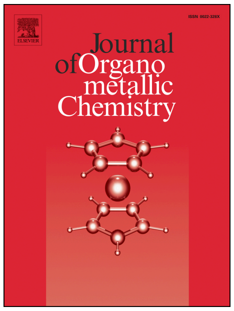

Amine adducts of (4-ClC$_6$H$_4$)$_3$B$_3$O$_3$, Lewis acidity of triarylboroxines, and an XRD study on the related tetraphenylboroxinate(1-) salt, [C$_6$H$_{11}$NMe$_3$][Ph$_4$B$_3$O$_3$]

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Amine adducts of (4-ClC$_6$H$_4$)$_3$B$_3$O$_3$, Lewis acidity of triarylboroxines, and an XRD study on the related tetraphenylboroxinate(1-) salt, [C$_6$H$_{11}$NMe$_3$][Ph$_4$B$_3$O$_3$].

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ABSTRACT

The stoichiometric reactions of amines with tri(4-chlorophenyl)boroxine (CPB) led to the formation of adducts CPB·L {L = morpholine (**1a**), benzylamine **(1b)** cyclohexylamine (**1c**), 2-picoline (**1d**), 4-picoline (**1e**), piperidine (**1f**)} and $(CPB)_2$·(4,4'-trimethylenedipiperidine) (**1g**). Compounds **1a**-**1g** have been characterised by NMR (^{11}B, ^{1}H, ^{13}C), IR spectroscopy and powder-XRD. VT ^{1}H NMR spectra on **1a** and **1d**-**1g** were consistent with a ligand exchange/recombination process and activation energies of 49 – 58 kJmol^{-1} were obtained. The synthesis of $[C_6H_{11}NMe_3][Ph_4B_3O_3]$ (**2**) from Ph_2BOBPh_2, $PhB(OH)_2$ and $[C_6H_{11}NMe_3][OH]$ in a 1:4:2 ratio in MeOH/H_2O is also reported. Compound **2** was characterized by thermal analysis (TGA/DSC), spectroscopy (IR, NMR) and **1a**, **1b** and **2** were further characterized by single-crystal XRD studies.

Keywords:

Boroxine, Tri(4-chlorophenyl)boroxine; Triarylboroxine; Tetraphenylboroxinate(1-); VT NMR; XRD structures.

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1. Introduction

Adducts of triarylboroxines with *N*-donor ligands are well documented with the first report appearing in 1933 [1]. A few years later, Burg reported the syntheses of 1:1 adducts of ammonia and trimethylamine with trimethylboroxine [2]. In 1958, Snyder *et al.* [3] proposed that the structure of these adducts involved the coordination of the nitrogen atom of the ligand to one of the boron atoms in the boroxine rings (Figure 1a) and since then there have been several reports of 1:1 adducts of triarylboroxines with *N*-donor ligands [4-22]. Diamine ligands have been reported to bridge between two boroxine acceptors [4] and *N*-donor ligand / boroxine stoichiometric ratios other than 1 / 1 have also been investigated [4, 6, 23]. The structures of these adducts and their applications in batteries, COFs and NLO materials have been recently reviewed [14]. Triarylboroxine adducts have been studied through ^{1}H NMR spectroscopy in solution, and in 1968 Ritchey [5] concluded that at room temperature the three boron centres were equivalent. Yalpani and Boese [6] reinvestigated these systems using variable temperature (VT) ^{1}H NMR studies and concluded that in solution there is a temperature dependent fluctuation of the amine between the three borons of the boroxine ring. More recent VT NMR studies concluded that neither steric congestion [7] nor electronic effects of the aryl rings of the triarylboroxines [8] dominate $\Delta G^‡$ for this ligand exchange process and that it is likely to be associated with disruption of the B-O π-system [7, 8]. Computational work on the formation of boroxines from boronic acids and their adducts have also been reported [13, 18, 24]. This manuscript describes the preparation of some previously unreported amine adducts of tri(4-chlorophenyl)boroxine (CPB). In order to gain further insight into the ligand dissociation/recombination process occurring in solution in these complexes we have studied several CPB complexes by VT ^{1}H NMR. Single-crystal XRD structures of two examples are also reported, together with the synthesis and XRD structure of a related tetraphenylboroxinate(1-) salt,

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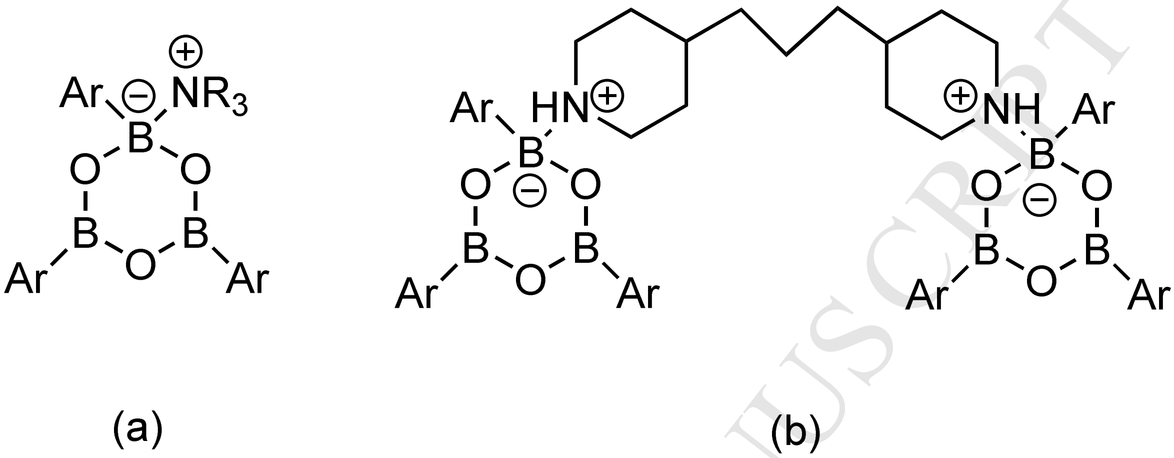
[trimethyl(cyclohexyl)ammonium][$Ph_4B_3O_3$].



(a)

(b)

Figure 1. (a) Schematic drawing of a 1:1 triarylboroxine.amine adduct: Ar = 4-ClC_6H_4, amine = morpholine (**1a**), benzylamine (**1b**) cyclohexylamine (**1c**), 2 -picoline (**1d**), 4-picoline (**1e**), piperidine (**1f**) and (b) 2:1 adduct Ar = 4-ClC_6H_4 (**1g**).

2. Experimental

2.1 General

All chemicals were obtained commercially. (4-$ClC_6H_4)_3B_3O_3$ was obtained by dehydration (oven 100 °C, 24h) of the commercially available boronic acid, 4-$ClC_6H_4B(OH)_2$. NMR spectra were obtained on a Bruker Avance-400 spectrometer with ^1H, ^{11}B, ^{13}C, and ^{31}P spectra ($CDCl_3$ unless stated otherwise) obtained at 400, 128, 101, and 162 MHz, respectively. NMR data are reported in ppm with positive chemicals shifts (δ) to high frequency (downfield) of TMS (^1H, ^{13}C), $BF_3{\cdot}OEt_2$ (^{11}B) and H_3PO_4 (^{31}P). Infra-Red spectra were obtained as KBr pellets on a Perkin-Elmer FTIR spectrometer over 450-4000 cm^{-1}. TGA and DSC analysis was performed (in air) between 10 and 800 °C on a SDT Q600 V.4.1

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Build 59 instrument using Al_2O_3 crucibles, with a ramp rate of 10 ^{o}C per minute. Powder XRD data were obtained on a Philips 1050/37 X-ray diffractometer equipped with an iron filter, using Cu-Kα radiation (λ = 0.154056 nm) with a continuous scan between $2\theta = 5^{o}$-75^{o} and Philips X'Pert software. CHN analysis was carried out at OEA Laboratories Ltd, Callington, Cornwall. Single crystal X-ray crystallography was carried out at the EPSRC National Crystallographic Service at the University of Southampton.

2.2 Preparation of triarylboroxine.amine adducts.

The triarylboroxine·amine adducts were all prepared using a general procedure [10], as detailed in Section 2.2.1 for compound **1a**.

*2.2.1 Preparation of tri(4-chlorophenyl)boroxine.morpholine, CPB.C_4H_9NO (**1a**).*

Morpholine (0.11g, 1.25 mmol) was added to a stirred suspension of $(4\text{-}ClC_6H_4)_3B_3O_3$ (0.50 g, 1.20 mmol) in Et_2O (20 ml), under an dry N_2 atmosphere. After the solid dissolved (approximately 10 minutes) the solution was filtered and the solvent removed under vacuum. The resulting white solid product was recrystallized from $CHCl_3$ (0.55 g, 92% yield). Mp: 217 – 220 °C. Elemental Anal. Calc. (%) for $C_{22}H_{21}B_3Cl_3NO_4$: C, 52.6; H, 4.2; N, 2.8. Found (%): C, 52.4; H, 4.3; N, 2.8. NMR ($CDCl_3$, RT). ^{1}H δ/ppm: 3.05-3.12 (br m, 5H), 3.78 (br s, 4H), 7.37 (d, 6H), 7.90 (d, 6H). ^{13}C δ/ppm: 44.43 ($2CH_2$), 66.09 ($2CH_2$), 128.04 (6CH), 135.44 (6CH). ^{11}B δ/ppm: 21.0. IR (KBr disk) ν_{max}/cm^{-1}: 3437 (br), 3214 (vs), 3070, 3026, 2982, 2854 (m), 1591 (vs), 1484 (s), 1433 (s), 1410 (s), 1374 (m), 1326 (s), 1280 (s), 1248 (m), 1191 (s), 1125 (s), 1088 (s), 1044 (m), 1012 (s), 889 (m), 848 (m), 812 (s), 766 (s), 727 (m), 664 (s), 624, 538, 452 (s). p-XRD: d spacing/Å (% rel. int.): 5.43 (100), 3.45 (95), 3.63 (77), 3.82 (68), 5.36 (54), 5.47 (53).

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*2.2.2 Preparation of tri(4-chlorophenyl)boroxine.benzylamine, CPB.C_7H_9N (**1b**).*

0.61 g, 98% yield. Mp: 155 – 157 °C. Elemental Anal. Calc. (%) for $C_{25}H_{21}B_3Cl_3NO_3$: C, 57.5; H, 4.1; N, 2.7. Found (%): C, 57.1; H, 4.1; N, 2.7. NMR ($CDCl_3$, RT). ^1H δ/ppm: 3.72 (s, br, NH_2), 3.93 (s, 2H, CH_2), 7.18 (m, 2H), 7.34 – 7.41 (m, 9H), 7.94 (d, 6H). ^{13}C δ/ppm: 45.11 (CH_2), 128.08 (CH), 128.19 (CH), 129.15 (CH), 135.23 (CH), 136.26 (C). ^{11}B δ/ppm: 19.8. IR (KBr disk) ν_{max}/cm^{-1}: 3434 (br), 3274 (s), 3205 (s, br), 3219 (s, br), 3067 (s), 3033 (s), 1920 (s), 1593 (vs, br), 1402 (s), 1376 (s), 1344 (s), 1324 (s), 1289 (s, br), 1243 (s), 1206 (m), 1115 (s), 1083 (s, br), 1050 (m), 1014 (s), 992 (s), 958, 938, 916, 881 (m, br), 822 (s, br), 775 (s), 732 (s), 700 (s), 669 (s), 628, 604, 541 (m), 522 (m), 480 (m), 453 (s). p-XRD: d spacing/Å (% rel. int.): 3.98 (100), 3.38 (92), 4.69 (58) 2.03 (69).

*2.2.3 Preparation of tri(4-chlorophenyl)boroxine.cyclohexylamine, CPB.$C_6H_{13}N$ (**1c**).*

0.51 g, 89% yield. Mp: 177 – 181 °C. Elemental Anal. Calc. (%) for $C_{24}H_{25}B_3Cl_3NO_3$: C, 56.1; H, 4.9; N, 2.7. Found (%): C, 54.7; H, 4.8; N, 2.5. NMR ($CDCl_3$, RT). ^1H δ/ppm: 1.09-1.26 (m, 5H), 1.59 (d, 1H), 1.70 (d, 2H), 1.98 (d, 2H), 2.97 (m, 1H), 3.55 (br s, 2H), 7.38 (d, 6H), 7.90 (d, 6H). ^{13}C δ/ppm: 24.31 ($2CH_2$), 24.91 (CH_2), 33.50 ($2CH_2$), 51.22 (C), 128.04 (6CH), 135.20 (6CH), 136.21 (C-Cl). ^{11}B δ/ppm: 22.2. IR (KBr disk) ν_{max}/cm^{-1}: 3436 (br), 3275 (m), 3233 (m), 3072 (w), 2935 (s, br), 2858 (s), 1592 (s), 1562 (m), 1434 (m), 1408 (s), 1376 (m), 1339 (m), 1327 (m), 1285 (s, br), 1243 (m), 1189 (m), 1120 (m), 1081 (s), 1013 (s), 982 (m), 821 (s), 765 (s, br), 733 (m), 662 (m), 582, 451 (s). p-XRD: d spacing/Å (% rel. int.): 3.48 (100), 4.72 (78), 4.12 (55), 4.01 (48), 4.40 (47), 4.89 (44).

*2.2.4 Preparation of tri(4-chlorophenyl)boroxine.2-picoline CPB.C_6H_7N (**1d**).*

0.44 g, 72% yield. Mp: 289 – 291 °C. Elemental Anal. Calc. (%) $C_{24}H_{19}B_3Cl_3NO_3$: C,

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56.7; H, 3.8; N, 2.8. Found (%): C, 56.2; H, 3.8; N, 2.2. NMR ($CDCl_3$, RT). ^1H δ/ppm: 2.75 (s, 3H, CH_3), 7.30 (d, 1H), 7.38 (m, 7H), 7.81 (t, 1H), 7.92 (d, 6H), 9.07 (d, 1H). ^{13}C δ/ppm: 23.56 (CH_3), 122.13 (CH), 126.84 (CH), 128.15 (CH), 135.80 (CH), 136.97 (C-Cl), 139.44 (CH), 146.19 (CH), 157.94 (C). ^{11}B δ/ppm: 23.4. IR (KBr disk) ν_{max}/cm^{-1}: 3436 (br), 3071, 3035, 2940, 1620 (m), 1594 (s), 1563 (m), 1485 (m), 1406 (s, br), 1374 (m, br), 1344 (s, br), 1327 (s, br), 1294 (s, br), 1283 (s, br), 1121 (s), 1082 (s, br), 1043 (m, br), 1014 (s), 977 (m), 822 (m), 808 (m), 760 (s, br), 740 (s, br), 694 (m), 613 (s), 457 (s). p-XRD: d spacing/Å (% rel. int.): 5.47 (100), 3.63 (61), 3.49 (53), 11.12 (49), 3.70 (39), 5.27 (35).

*2.2.5 Preparation of tri(4-chlorophenyl)boroxine.4-picoline, CPB.C_6H_7N (**1e**).*

0.59 g, 97% yield. Mp: 192 – 195 °C. Elemental Anal. Calc. (%) $C_{24}H_{19}B_3Cl_3NO_3$: C, 56.7; H, 3.8; N, 2.8. Found (%): C, 56.7; H, 3.7; N, 2.7. NMR ($CDCl_3$, RT). ^1H δ/ppm: 2.50 (s, 3H, CH_3), 7.35 (d, 6H), 7.42 (d, 2H), 7.93 (d, 6H), 8.80 (d, 2H). ^{13}C δ/ppm: 21.72 (CH_3), 126.61 (CH), 127.94 (CH), 135.14 (CH), 143.03 (CH). ^{11}B δ/ppm: 19.9. IR (KBr disk) ν_{max}/cm^{-1}: 3434 (br), 3072, 3029, 1633 (m), 1593 (s, br), 1563 (m), 1485 (m), 1433 (s, br), 1407 (s, br), 1378 (m, br), 1325 (s, br), 1278 (s), 1246 (s), 1206 (s), 1179 (m), 1118 (m), 1081 (s, br), 1043 (m), 1014 (s), 984 (s), 854 (m), 822 (m), 803 (m), 762 (s, br), 743, 732, 696 (m), 660 (m), 636 (m), 508 (m), 453 (s). p-XRD: d spacing/Å (% rel. int.): 4.62 (100), 5.39 (78), 3.46 (56), 3.58 (44), 4.97 (36), 3.25 (27).

*2.2.6 Preparation of tri(4-chlorophenyl)boroxine.piperidine, CPB.$C_5H_{11}N$ (**1f**).*

0.59 g, 98% yield. Mp: 127 – 130 °C. Elemental Anal. Calc. (%) for $C_{23}H_{23}B_3Cl_3NO_3$: C, 55.2; H, 4.6; N, 2.8. Found (%): C, 55.1; H, 4.6; N, 2.8. NMR ($CDCl_3$, RT). ^1H δ/ppm: 1.66 (s, br, 6H), 2.80 (s, br, 5H), 7.37 (d, 6H), 7.91 (d, 6H). ^{13}C δ/ppm: 23.05 (CH_2), 25.37 (CH_2), 127.90 (CH), 135.44 (CH). δ_B (ppm):24.6.IR (KBr disk) ν_{max}/cm^{-1}:

3520 (br), 3223 (vs), 3069 (m), 3026, 2956 (m, br), 2870 (m), 1912, 1591 (vs), 1484 (s), 1435 (s, br), 1410 (s, br), 1376 (m, br), 1326 (s, br), 1282 (s, br), 1246 (s, br), 1188 (s), 1121 (s), 1085 (s, br), 1044 (m), 1012 (s), 971 (m), 868 (m), 810 (s), 766 (s, br), 728 (m), 662 (s), 614 (m), 512, 477, 450 (s). p-XRD: d spacing/Å (% rel. int.): 3.54 (100), 3.55 (70), 3.67 (39), 3.68 (39), 3.95 (34), 3.18 (30).

*2.2.7 Preparation of bis(tri(4-chlorophenyl)boroxine).4,4'-trimethylenedipiperidine, $(CPB)_2.C_{13}H_{26}N_2$ (**1g**).*

1.72 g, 92 % yield. Mp: 247 – 250 °C. Elemental Anal. Calc. (%) for $C_{31}H_{38}B_3Cl_3N_2O_3$: C, 56.6; H, 4.8; N, 2.7. Found (%): C, 56.3; H, 4.8; N, 2.6. NMR ($CDCl_3$, RT). ^{1}H δ/ppm: 1.06-1.23 (m, 10H), 1.35 (br s, 2H), 1.82 (d, 4H), 2.55 (br s, 4H), 2.75 (br s, 2H), 3.38 (br s, 4H), 7.36 (d, 12H), 7.88 (br s, 12H). ^{13}C δ/ppm: 23.28, 31.56, 34.45, 36.19, 45.14. ^{11}B δ/ppm: not obtained. IR (KBr disk) ν_{max}/cm^{-1}: 3415 (br), 3229 (m), 3072 (m), 3031 (m), 2928 (m), 2856 (m), 1592 (vs), 1562 (s), 1486 (s), 1435 (s), 1415 (s), 1380 (m), 1330 (m), 1278 (s), 1247 (m), 1196 (s), 1172 (s), 1120 (s), 1097 (s), 1083 (s), 1044 (s), 1014 (vs), 985 (m), 972 (m), 857(m), 828 (m), 816 (m), 769 (s), 733 (m), 670 (m), 663, 629, 612. p-XRD: d spacing/Å (% rel. int.): amorphous solid.

2.3 Lewis acidity measurements of triarylboroxines.

The Et_3PO (TEPO) adduct of tri(4-chlorophenyl)boroxine, CPB.TEPO, was prepared *in situ* in an NMR tube by the addition of a slight excess of CPB to TEPO dissolved in $CDCl_3$ (0.5 mL). NMR ($CDCl_3$, RT). ^{1}H δ/ppm: 1.15 – 1.23 (m, 9H, $3CH_3$), 1.78 – 1.87 (m, 6H, $3CH_2$), 7.35 – 7.47 (m, 6H, 6CH), 7.76 – 8.10 (m, 6H, 6CH). ^{13}C δ/ppm: 5.66 (d, ^2J = 4.7 Hz, CH_3), 18.96 (d, ^1J = 67.6 Hz, CH_2), 128.45 (CH arom.), 136.77 (CH arom.). ^{11}B δ/ppm: 29.1. ^{31}P δ/ppm: 62.0 (AN = 46).

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*2.4 Preparation of [$C_6H_{11}NMe_3$][$Ph_4B_3O_3$] (**2**)*

[$C_6H_{11}NMe_3$]I (2.16 g, 8.01 mmol) was dissolved in water (50 ml) and the Dowex 550Å monosphere resin (OH^- form) was added to the solution which was stirred for 48 h. The resin was removed by filtration and the solvent was removed from the filtrate by rotary evaporation to give an oil. The oil was made up to 100 ml in a 1:1 methanol/water solution and an aliquot of this solution (25 ml, containing 2 mmol) was reacted with $PhB(OH)_2$ (0.47g, 3.86 mmol) and Ph_2BOBPh_2 (0.34 g, 0.98 mmol). The solvent was then removed (*via* rotary evaporation/suction filtration) to yield the product, [$C_6H_{11}NMe_3$][$Ph_4B_3O_3$] (**2**), as a white powder (0.77g, 75%) . M.p. 220 - 225°C. Elemental Anal. Calc. for $C_{33}H_{20}B_3O_3N$: C, 74.6; H, 7.6; N, 2.6. Found: C, 74.5; H, 7.6; N, 2.6. NMR (acetone-d_6, RT): ^1H δ/ppm: 1.18 (q, 1H), 1.35 (q, 2H), 1.52 (q, 2H), 1.63 (d, 1H), 1.92 (d, 2H), 2.28 (d, 2H) 3.15 (s, 9H), 3.37 (t, 1H), 6.80 (t, 2H), 7.05 (t, 4H), 7.30 (m, 6H), 7.75 (d, 4H), 8.22 (m, 2H). ^{13}C δ/ppm: 24.35, 25.06, 25.93, 50.56, 75.25, 123.15, 125.75, 126.88, 129.08, 131.72, 134.59. ^{11}B δ/ppm: 3.4 (1B), 26.9 (2B). IR (KBr disk) ν_{max}/cm^{-1}: 3068 (w), 3012 (w), 2859 (w), 1598 (m), 1469 (m), 1448 (vs), 1421 (s), 1355 (m), 1274 (m), 1231 (vs), 1162 (m), 1145 (m), 1110 (m), 1064 (m), 1025 (m), 953 (m), 867 (m), 770 (m), 751 (m), 702 (vs), 676 (s), 620 (m), 572 (s). TGA: oxidation of organics to leave $1.5B_2O_3$ (220-390 ^oC): residue 20.1% (calc 19.7%). The crude product was recrystallized from acetone to give small (colourless) crystals suitable for an XRD analysis.

*2.5 XRD analysis of **1a**, **1b**, and **2**.*

XRD data Crystallographic data for compounds **1a**, **1b** and **2** are given in Table 1. The crystallographic data collection of compounds were performed on either a Rigaku AFC12 goniometer equipped with an enhanced sensitivity HG Saturn 724+ detector mounted

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at the window on an FR-E+ SuperBright molybdenum rotating anode generator with either HF Varimax optics (compound **1a**) or VHF Varimax optics (compound **1b**) or a Rigaku 007-HF copper rotating anode with AFC11 goniometer with Saturn944+ CCD area detector (compound **2**) all at 100(2) K. Cell determinations and data collections were carried out using CrystalClear [25]. With the data reduction, cell refinement and absorption correction using CrysAlisPro [26]. Using Olex2 [27] the structures were solved using SHELXT [28] and models refined with SHELXL [29]. H1 in 1**a** was allowed to freely refine as it is involved in hydrogen bonding and all other hydrogen atoms were refined in riding positions.

Table 1. Crystal data and structure refinement for compounds **1a**, **1b**, and **2**.

Compound	**1a**	**1b**	**2**
Empirical formula	$C_{22}H_{21}B_3Cl_3NO_4$	$C_{25}H_{21}B_3Cl_3NO_3$	$C_{33}H_{40}B_3NO_3$
Formula weight	502.18	522.21	531.09
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71075 Å	0.71075 Å	1.54187 Å
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	P–1	P–1	$Pca2_1$
Unit cell dimensions	a = 8.8330(2) Å b = 11.7778(2) Å c = 12.3245(3) Å α = 81.153(2)° β = 76.271(2)° γ = 68.541(2)°	a = 10.8662(3) Å b = 11.6419(4) Å c = 21.0508(4) Å α = 88.316(2)° β = 89.333(2)° γ = 70.864(2)°	a = 34.3666(1) Å b = 19.9735(1) Å c = 17.2662(1) Å α = 90° β = 90° γ = 90°
Volume	1156.00(5) Å^3	2514.75(12) Å^3	11851.89(10) Å^3
Z	2	4	16
Density (calculated)	1.443 Mg / m^3	1.379 Mg / m^3	1.191 Mg / m^3
Absorption coefficient	0.427 mm^{-1}	0.393 mm^{-1}	0.567 mm^{-1}
F(000)	516	1072	4544
Crystal	Block; Colourless	Lath; Colourless	Plate; Colourless
Crystal size	0.130 × 0.080 × 0.050 mm^3	0.170 × 0.040 × 0.010 mm^3	0.48 × 0.40 × 0.04 mm^3
Reflections collected	20528	32418	85957
Independent reflections	5284 [R_{int} = 0.0220]	11479 [R_{int} = 0.0236]	18721 [R_{int} = 0.0231]
Data / restraints / parameters	5284 / 0 / 302	11479 / 0 / 631	18721 / 1 / 1454
Goodness-of-fit on F^2	1.040	1.023	1.079
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1$ = 0.0288, $wR2$ = 0.0754	$R1$ = 0.0461, $wR2$ = 0.1108	$R1$ = 0.0321, $wR2$ = 0.0810
R indices (all data)	$R1$ = 0.0324, $wR2$ = 0.0775	$R1$ = 0.0613, $wR2$ = 0.1192	$R1$ = 0.0333, $wR2$ = 0.0819
Absolute structure parameter	n/a	n/a	0.03(4)
Largest diff. peak and hole	0.405 and –0.225 e Å^{-3}	1.467 and –0.877 e Å^{-3}	0.410 and –0.199 e Å^{-3}

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3. Results and discussion

3.1 Formation of amine complexes of tri(4-chlorophenyl)boroxine

One to one amine adducts of tri(4-chlorophenyl)boroxine (CPB) were readily prepared by the direct interaction of the organic base with a suspension of the boroxine in Et_2O (Scheme 1). The CPB is insoluble Et_2O, but the suspension readily dissolved upon addition of amines to form pale yellow solutions of the products, which were isolated in high yields after removal of the solvent and recrystallization of the residue. Six adducts, formulated as PCB.L {L = morpholine (**1a**), benzylamine (**1b**), cyclohexylamine (**1c**), 2-picoline (**1d**), 4-picoline (**1e**), piperidine (**1f**)} based on elemental analysis data, spectroscopic analysis (NMR) and from single crystal XRD studies on representative samples (**1a**, **1b**), were prepared. The IR spectra of compounds **1a**-**1f** all show strong very strong bands in the region 1500-1200 cm^{-1} assigned to B-O stretches of the boroxole ring [3, 9, 30]. The X-ray structures of **1a** and **1b** (Section 3.2) clearly demonstrate that they are 1:1 adducts and that the amine ligands are coordinated to one the three boron centres of the CPB rings.

Compounds **1a**-**1f** were air-stable, white solids with clearly defined melting points. These solids were readily soluble in chlorinated solvents, but less soluble in Et_2O and petroleum ether. CPB was also reacted with 4,4’-trimethylenedipiperidine in a 2:1 stoichiometric ratio to form a 2:1 adduct (Scheme 1).

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$$(4\text{-}ClC_6H_4)_3B_3O_3 + L \rightarrow (4\text{-}ClC_6H_4)_3B_3O_3\cdot L\ \ (\mathbf{1a\text{-}f})$$

{L = morpholine (**1a**), benzylamine (**1b**), cyclohexylamine (**1c**), 2-picoline (**1d**), 4-picoline (**1e**), piperidine (**1f**)}

$$2(4\text{-}ClC_6H_4)_3B_3O_3 + L \rightarrow \{(4\text{-}ClC_6H_4)_3B_3O_3\}_2\cdot L\ \ (\mathbf{1g})$$

{L = 4,4’-trimethylenedipiperidine}

Scheme 1

*3.2 XRD structural studies on tri(4-chlorophenyl)boroxine·morpholine (**1a**) and tri(4-chlorophenyl)boroxine·benzylamine (**1b**).*

The solid-state structures of **1a** and **1b** confirm their formulations as 1:1 adducts. Compound **1a** has one unique molecule within its asymmetric unit whereas the asymmetric unit of **1b** contains two independent molecules. The bond distances and angles in the two molecules of **1b** are generally not significantly different and their gross structures are the same; for brevity only dimensions of the molecule containing B1 are discussed here. Full bond distance and bond angle details are available for **1a** and **1b** in the Supplementary Information. The crystallographically determined structures confirm that they are both 1:1 amine adducts of tri(4-chlorophenyl)boroxine, and the structures of **1a** and **1b** are shown in Figures 2 and 3, respectively. Bond lengths and angles associated with the boroxole (B_3O_3) rings are given in the captions to these Figures. The boroxole rings of the adducts in **1a** and **1b** contain two three-coordinate trigonal planar boron centres (B2 and B3), three two-coordinate angular oxygen atoms (O1, O2, and O3), and a tetrahedral four-coordinate boron centre (B1). These almost planar boroxole rings adopt an envelope conformation, with B1 being 0.0906(16) Å (**1a**) and 0.150(3) Å (**1b**) away from the best plane of O1, O2 and O3.

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The four-coordinate boron (B1) in **1a** has a distorted tetrahedral geometry with bond angles in the range of 103.33(9) – 114.61(10)° and the three-coordinate boron atoms (B2 and B3) have bond angles in the range of 117.20(11) – 121.46(11)°. The three ring two-coordinate oxygen atoms have bond angles in the range of 119.34(10) – 122.18(10)°. The coordinated morpholine ligand is found to be in a chair conformation and there is an intermolecular H-bond between N1-H1 atom of the morpholine ligand an Cl2 atom of a neighbouring molecule {*d*(N-H) 0.869(17) Å; *d*(H···Cl), 2.512(17) Å; *d*(N···Cl), 3.3775(11) Å; < (NHCl), 174.3(14)^{o}}. A similar description can be applied to **1b** where angles about the distorted tetrahedral boron (B1) range from 104.85(15) – 114.00(16)°, the two trigonal boron atoms range from 118.29(18) – 121.03(18)° and three two-coordinate ring oxygen atoms range from 119.17(16) – 122.90(16)°. The aryl rings of the benzylamine ligand in **1b** sits close to perpendicular to the boroxole ring (79.13(7)°). The C-Cl bond lengths in **1a** {1.7444(12) - 1.7567(12) Å} are just longer than those observed in **1b** {1.7413(19) - 1.746(2) Å}. The B-N and B-O bond lengths in **1a** and **1b** (see captions to Figures 2 and 3) are consistent with bond lengths observed in other amine triarylboroxine adducts [4, 6-13, 15, 16], amine adducts of related BOSi ring systems [31, 32], and tetraorganylboroxinate(1-) [33-36] systems. The B-O distances are described in more detail in Section 3.5.

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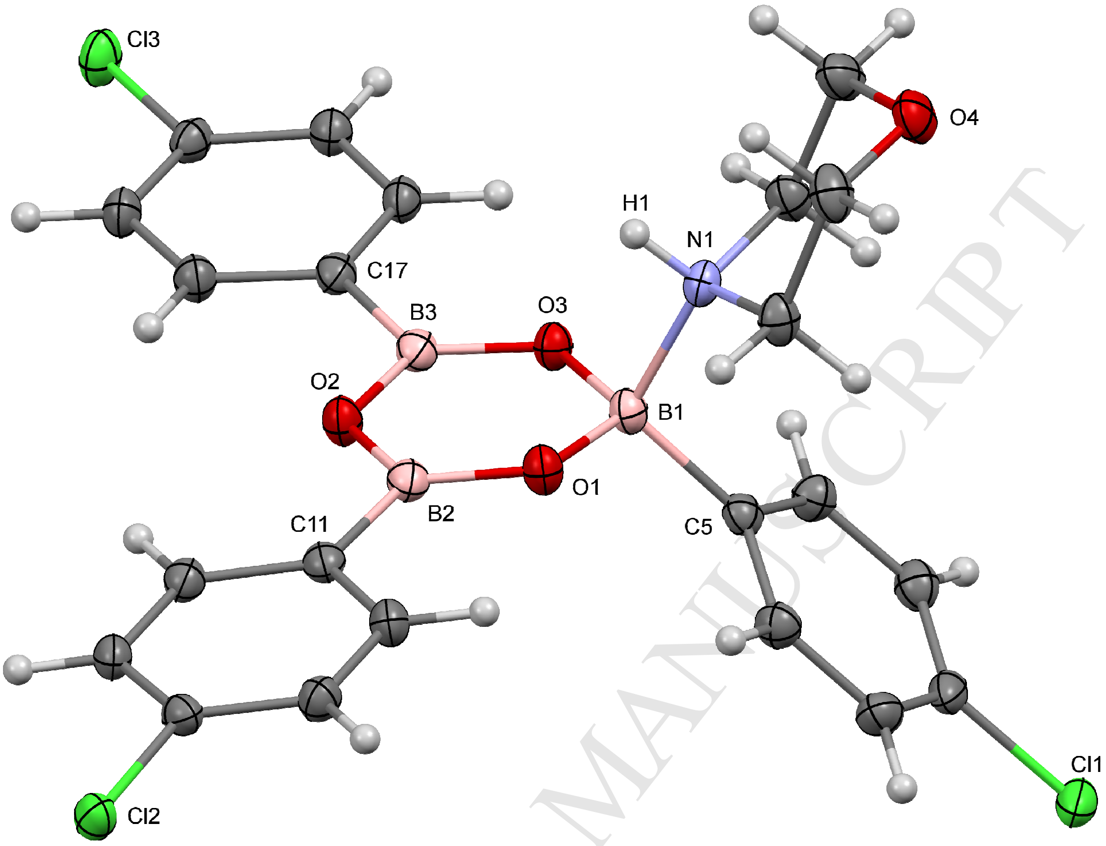

Figure 2. Drawing of the molecular structure of tri(4-chlorophenyl)boroxine·morpholine (**1a**), showing selected labelling. Distances (Å): B1-O1, 1.4551(15); O1-B2, 1.3473(16); B2-O2, 1.3836(16); O2-B3, 1.3849(16); B3-O3, 1.3519(16); O3-B1, 1.4621(15); B1-N1, 1.6543(16); B1-C5, 1.6073(18); B2-C11, 1.5655(18); B3-C17, 1.5684(18).

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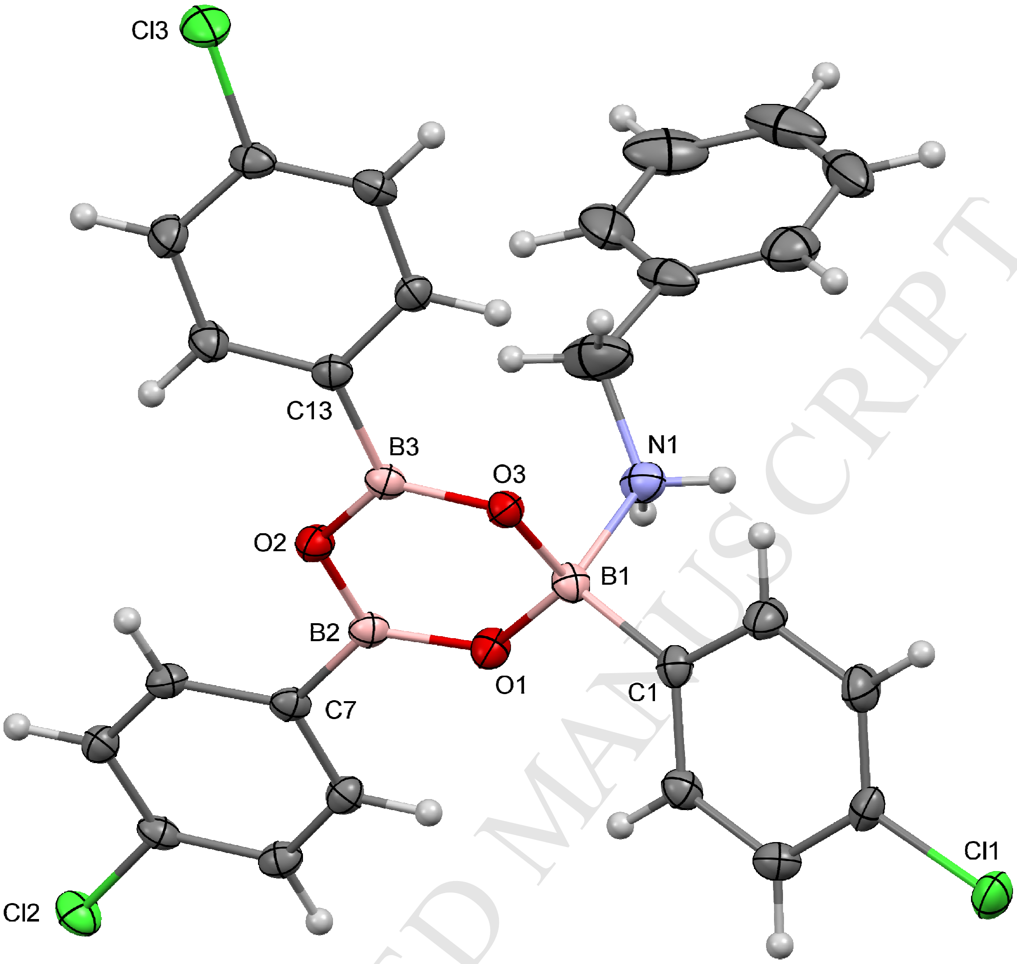

Figure 3. Drawing of one of the two independent molecules in the solid-state structure of tri(4-chlorophenyl)boroxine·benzylamime (**1b**), showing selected labelling. Distances (Å): B1-O1, 1.450(3); O1-B2, 1.352(3); B2-O2, 1.390(3); O2-B3, 1.386(3); B3-O3, 1.362(3); O3-B1, 1.458(2); B1-N1, 1.683(3); B1-C1, 1.608(3); B2-C7, 1.568(3); B3-C13, 1.563(3).

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3.3 Variable temperature 1H NMR studies on the ligand dissociation/recombination process.

At first sight the ^{1}H and ^{13}C data of the **1a-1g** are inconsistent with the XRD structures since at room temperature all adducts displayed three equivalent CPB aryl rings and not the expected 2:1 signals. However, this has been noted before in related compounds

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and has been explained by a fluxional process involving rapid (at room temperature) ligand exchange [5-12]. Room temperature solution $^{11}B\{^{1}H\}$ NMR spectra of **1a-1g** gave a broad weak signals in the range of 20-23 ppm for the 1:1 adducts, and were consistent with data on related systems [5-12]. These chemical shifts are indicative of a weighted average, associated with ligand exchange, situated in between that expected for a three coordinate boron signal (*ca*. 30 ppm) and a four coordinate boron signal (*ca*. 4 ppm). Variable temperature ^{1}H NMR spectroscopy (+35 to -35 °C, 5 °C intervals) on **1a**, **1d**, **1e**, **1f** and **1g** was undertaken in $CDCl_3$ in order to further characterize the ligand exchange process. The aromatic region of **1g** is shown in Figure 4 as a representative example.

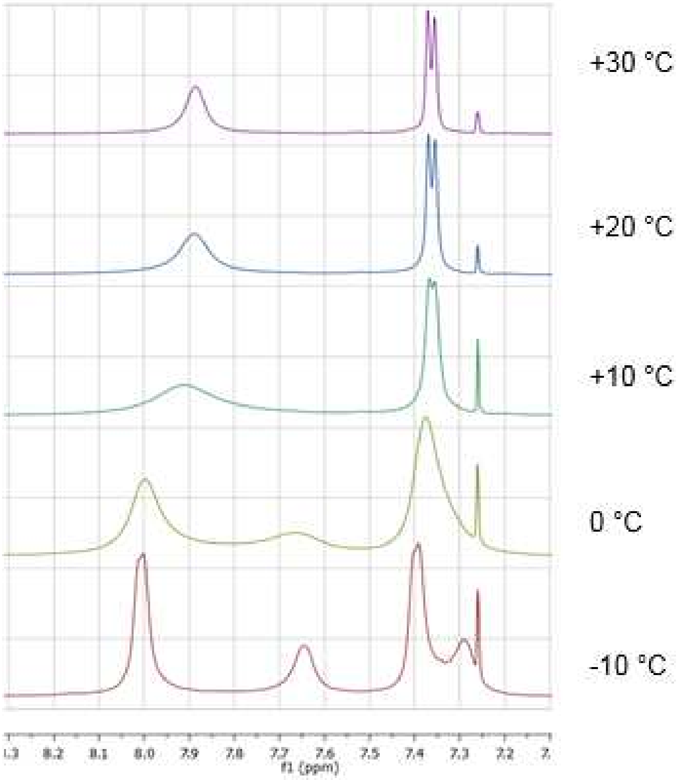

Figure 4. Variable temperature ^{1}H NMR signals of the aryl substituents on tri(4-chlorophenyl)boroxine in **1g**.

At -10 °C the aryl rings protons of **1g** appear as four separate signals at 7.29, 7.39, 7.65 and 8.00 ppm, with the relative intensities 8:4:8:4 and consistent with slow ligand exchange relative to the NMR timescale. Upon warming, the two upfield signals (associated with protons which are at the *meta* to the boron atoms) broaden, coalesce at -5 °C, and then sharpen into a doublet at 7.37 ppm. Likewise, the two lower-field signals (associated with protons at the *ortho* to the boron atoms) broaden, coalesce at +5 °C, and then sharpen into a broad singlet upon warming. The Gibbs free energy of activation ($\Delta G^{\ddagger}$) for a 1:1 ligand exchange process can be calculated [37] from the ligand-exchange rate (k) at coalescence temperature (T_c) and the low temperature peak separation at slow-exchange (δ_v). This approach is strictly only correct for a 1:1 site exchange [12] although can give useful approximations for 2:1 systems. The calculated $\Delta G^{\ddagger}$ data for **1a**, **1e**, **1f** and **1g** can be found in Table 2. Data was not available for **1d** since slow exchange was not observed in the ^{1}H NMR spectra at -35 °C. The $\Delta G^{\ddagger}$ values obtained for these CPB·amine complexes lie in the range of 49-58 kJmol^{-1}. These data are at the high end of ranges reported for ligand exchange for various N-donor ligands at tri(3,5-dimethylphenyl)boroxine (MXB, 45-49 kJmol^{-1} [10]), tri(4-methylphenyl)boroxine (PTB, 43-46 kJmol^{-1} [10]), tri(2-methylphenyl)boroxine (OTB, 43-49 kJmol^{-1} [7]), tri(4-nitrophenyl)boroxine (MNB, 50 kJmol^{-1} [8]) and tri(4-bromophenyl)boroxine (PBB, 39-54 kJmol^{-1} [8]). Comparative data are available for morpholine as a ligand in **1a** for boroxines PBB, PTB and MXB; the activation energy for morpholine·PCB is calculated to be the highest, by 2-5 kJmol^{-1}. Likewise, data for **1e** can be directly compared with that for 4-picoline·OTB and **1e** is higher by 5 kJ mol^{-1}. However, these differences are likely to be within experimental error and may not indicate possible trends.

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Compound	**T_c** (K)	**δ_v** (Hz)	***k*** (s^{-1})^a	**$\Delta G^‡$** ($kJmol^{-1}$)^b
1a^c	255	50	111	54
1a^d	260	160	355	51
1e^c	258	95	211	51
1e^d	253	225	500	49
1f^c	283	55	122	58
1f^d	293	175	389	57
1g^c	268	50	111	55
1g^d	278	175	389	54

Table 2. Variable temperature ^{1}H NMR data. ^{a} $k = 2^{-1/2}\pi\delta_v$. ^{b}$\Delta G^‡ = -RTln(khk_B{}^{-1}T^{-1})$. ^{c} From upfield aromatic doublet of $(4\text{-}ClC_6H_4)_3B_3O_3{}^{\cdot}L$. ^{d} From downfield aromatic doublet of $(4\text{-}ClC_6H_4)_3B_3O_3{}^{\cdot}L$.

3.4 Measurement of Lewis acidity of $(4\text{-}ClC_6H_4)_3B_3O_3$

Gutmann's Acceptor numbers (AN) are generally accepted as useful way to assess the relative Lewis acidity of solvents [38, 39]. The AN of a particular solvent is calculated from $^{31}P\{^1H\}$ NMR chemical shifts of triethylphosphine oxide (TEPO) dissolved in that solvent. This scale has two fixed points, with the weak Lewis acid hexane at zero, and the strong Lewis acid antimony pentachloride at 100. A modification of this procedure, involving the synthesis of Et_3PO adducts of Lewis acids (often *in situ*), enables the acidity of the Lewis acid to be determined by a ^{31}P NMR measurement [40-42]. The Et_3PO adduct of CPB proved difficult to isolate following the synthetic procedures used above but nevertheless was prepared in *in situ*. The ^{31}P NMR shift of CPB$\cdot$Et$_3$PO (62.0 ppm) gave an AN number of 46, indicative of moderate Lewis acidity. This value slightly extends the AN range (49-51) reported for the triorganoboroxines $Ph_3B_3O_3$, $(4\text{-}BrC_6H_4)B_3O_3$ and $Me_3B_3O_3$ [9] and demonstrates that the 4-chlorophenyl groups have little effect on the Lewis acidity of the triarylboroxine. The CPB is a considerably weaker Lewis acid than the perfluorinated derivatives $(C_6F_5)_3B_3O_3$ (AN = 86) and $(C_6F_5)_3B$ (AN = 82), which contain the strongly electron withdrawing pentafluorophenyl groups [42-44].

*3.5 Synthesis of and XRD studies on trimethyl(cyclohexyl)ammonium tetraphenylboroxinate (**2**).*

The tetraryltriboroxinate(1-) anion is isoelectronic with Lewis base adducts of triarylboroxines, $Ar_3B_3O_3\cdot L$. Whilst there are many reported crystal structures of Lewis base adducts of boroxines, structures containing tetraryltriboxinate(1-) anions are much rarer and are limited to the following few examples: $[NMe_4][Ph_4B_3O_3]$ [33], $[(^tBu_3PAu)_4P][Ph_4B_3O_3]$ [34], $[Me_3NCH_2CH_2OH][Ph_3B_3O_3]$ [35], and $[Ph_2B\{OCH_2NMe(CH_2)_n\}_2][Ph_4B_3O_3]$ (n = 4, 5) [36]. $[(^tBu_3PAu)_4P][Ph_4B_3O_3]$ was prepared serendipitously, whereas the other salts were all prepared by the procedure first described by Rittig and co-workers [33]. Herein we report the synthesis of one further example in a salt containing the trimethyl(cyclohexyl)ammonium cation and report on its solid-state structure.

$[C_6H_{11}NMe_3][Ph_4B_3O_3]$ (**2**) was prepared in high yield following the method of Rittig and co-workers from Ph_2BOBPh_2, $PhB(OH)_2$ and $[C_6H_{11}NMe_3][OH]$ in a 1:4:2 ratio in MeOH/H_2O solution [33]. Compound **2** was characterized by satisfactory elemental analysis data, IR and NMR (^{1}H, ^{11}B, ^{13}C) spectroscopy, thermal analysis (TGA/DSC) and a single-crystal XRD study.

NMR spectra (room temperature) for **2** were recorded in *d*$_6$-acetone and ^{1}H and ^{13}C spectra were fully consistent with the anion and cation present. In particular, and in contrast to **1a-1g**, the ^{11}B spectrum of **2** showed two peaks, of relative intensity 2:1 and at chemical shifts expected for three-coordinate {O_2BC} and four-coordinate {O_2BC_2} centres [45].

The thermal properties of **2** were determined by TGA/DSC analysis in air over the temperature range of 25-800°C (see Supplementary Information). The salt decomposed in a single-stage process (220-390 °C) by oxidation (exothermic) of the organics present with the formation of B_2O_3. Oxidation of organics to leave B_2O_3 is always observed in the thermolysis of organic cation polyborates [46]. At the start of this decomposition process there is a small endothermic peak (230 ^{o}C) in the DSC trace and this corresponds to the sample's melting point.

The single-crystal XRD analysis showed that **2** is correctly formulated as a salt with discrete cations and anions, [$C_6H_{11}NMe_3$][$Ph_4B_3O_3$]. Within the unit cell there are 4 independent cations and 4 independent anions. These ions can be differentiated in the Supplementary Information with cations containing N121, N131, N141 or N151, and anions containing B1, B31, B61, or B91. A diagram of ions in containing N131 and the B1 is shown in Figure 5, and a discussion of the structure is restricted to this anion pair. The other independent ions within the structure are very similar and full details are available in Supplementary Information. The cyclohexyl ring of the cation adopts a chair conformation with the bulky trimethylamine group equatorial in all four of the independent cations.

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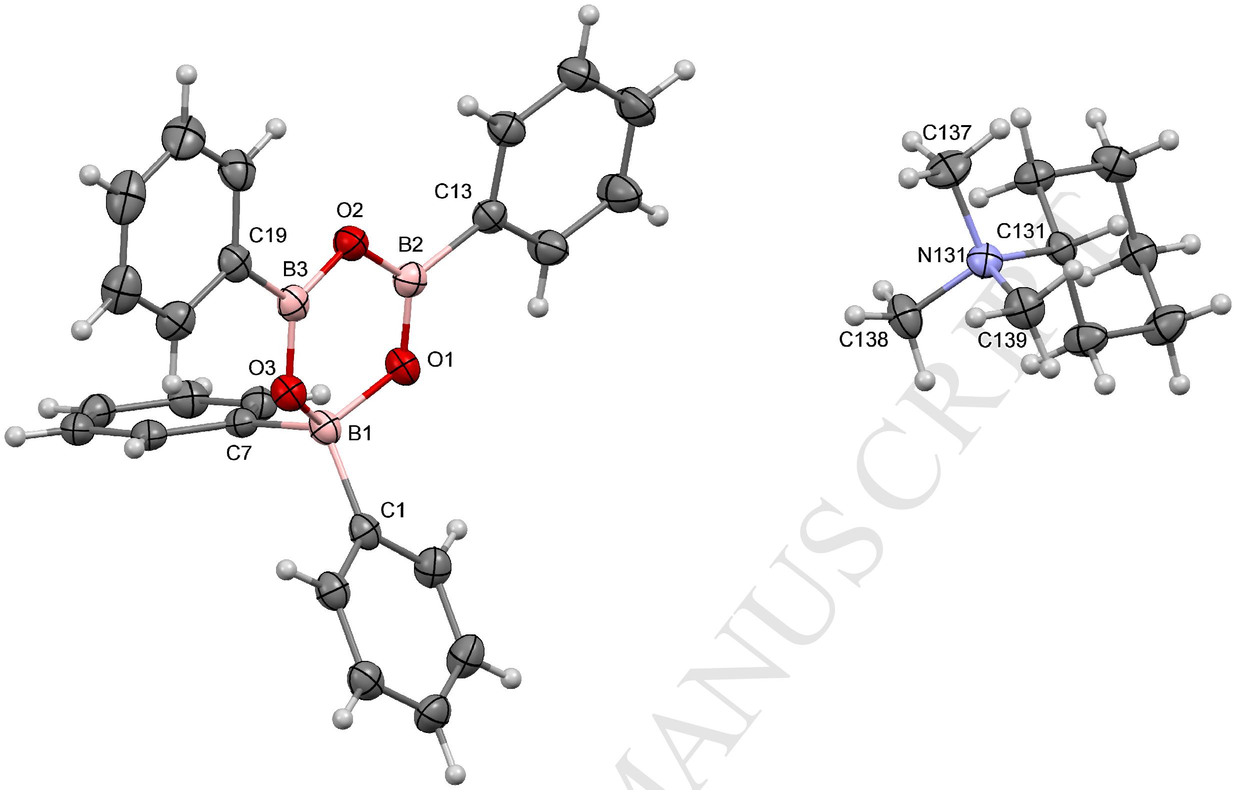

Figure 5. Drawing of one of the four independent cations and anions in the solid-state structure of trimethy(cyclohexyl)ammonium tetraphenylboroxinate(1-) (**2**), showing selected labelling. Distances (Å): B1-O1, 1.510(3); O1-B2, 1.332(3); B2-O2, 1.394(3); O2-B3, 1.399(3); B3-O3, 1.339(3); O3-B1, 1.500(3); B1-C1, 1.628(4); B1-C7, 1.630(3); B2-C13, 1.578(3); B3-C19, 1.569(3), N131-C131, 1.553(3), N131-C137, 1.498(3); N131-C138, 1.503(3); N131-C139, 1.498(3).

The tetraphenylboroxinate(1-) anion in **2** has the same gross boroxole ring structure as adducts **1a** and **1b**, with a neutral amine donor replaced by an anionic phenyl(1-) ligand. The boroxole ring adopts an envelope conformation with the four-coordinate boron (B1) out of the plane containing O1, O2 and O3 by 0.366(3) Å. The two B-C bond lengths of the four-coordinate bond are not significantly different from one another but these bonds are significantly longer than the B_{trig}-C bond lengths. These bond lengths and B-O ring distances are given in the caption to Figure 5. As has been noted previously for related structures [6, 10, 33], and confirmed here for structures **1a**, **1b** and **2**, there are significant differences in ring B-O bond lengths of the boroxole ring. In particular, B2-O1 and B3-O3 are significantly shorter than those found in the triarylboroxines PTB and $Ph_3B_3O_3$, (*ca*. 1.38 Å) [7, 47] and $Et_3B_3O_3$ [48] since adduct formation localizes B-O π-bonding between these pairs of atoms (Figure 6) as the B-O bonding at the tetrahedral B1 lengthens to a distance associated with a bond order of one.

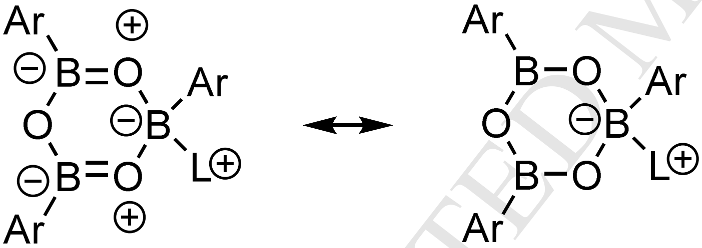

Figure 6. The resonance structure on the left makes an important contribution to the boroxole ring bonding in the tetraphenylboroxinate(1-) (Ar =Ph; L = Ph^-) anion in **2** and to the amine adducts of tri(4-chlorophenyl)boroxine, **1a** and **1b.**

4. Conclusions

A number of adducts of *N*-donor adducts of tri(4-chlorophenyl)boroxine (PCB) have been prepared and two examples (PCB·L, L = morpholine, cyclohexylamine), together with a tetraphenylboroxinate(1-) salt have been characterized crystallographically. These structures

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shown a variation of ring BO bond-lengths of the boroxole ring consistent with π-bonding between the oxygen atoms adjacent to the four-coordinate boron and the other two boron atoms. In solution, ligand dissociation / recombination occurs and this has been followed by variable temperature NMR spectroscopy. The experimentally determined $\Delta G^{\ddagger}$ values obtained for these CPB$\cdot$amine complexes lie in the range of 49-58 kJmol^{-1}, and although these data are at the high end of ranges reported for ligand exchange for other triarylboroxine adducts, such differences may be within experimental error and may not have significance.

Acknowledgements. We thank the EPSRC for the use of the NCS X-ray crystallographic service (Southampton).

Supplementary Information. Crystallographic data for **1a**, **1b**, **2** have been deposited with the Cambridge Crystallographic Data Centre with CCDC1810671, 1810673, 1810672. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ (fax +44 1223 336033) or email:deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk. Crystallographic data are also available as supplementary material.

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Highlights

Tri(4-chlorophenyl)boroxine (PCB) has moderate Lewis acidity (AN = 46).

Seven *N*-donor adducts of PCB have been synthesized.

Adducts undergo ligand dissociation/recombination in solution ($\Delta G^{\ddagger}$, 49–58 $kJmol^{-1}$).

XRD structures of two PCB adducts and $[(C_6H_{11})NMe_3][Ph_4B_3O_3]$ have been obtained.

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