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Complementary anion binding by bidentate boron-containing Lewis acids

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Abstract

Anion binding by the pyroborates $(catB)_2O$ (**1**, cat = $O_2C_6H_4$-1,2) and $(S,S\text{-}Ph_2C_2H_2O_2B)_2O$ (**2**) has been investigated by spectroscopic, structural and titration methods. **1** has been shown to act as a bifunctional Lewis acid, exemplified by the complementary (1:1) binding of bidentate bases such as acetate and dihydrogen phosphate. The former complex has been characterized in the solid state by X-ray diffraction and a binding constant of $1500 \pm 550\ M^{-1}$ determined in chloroform solution. The reaction of **2** with acetate, by contrast, leads to breakdown of the Lewis acid chelate and to the formation of the homochiral borate anion $[(S,S\text{-}Ph_2C_2H_2O_2)_2B]^-$ in good yield (84% based on the chiral component).

1. Introduction

The binding of anions by receptors based on three coordinate group 13 centres has been the subject of considerable recent research effort, with applications in anion abstraction, catalysis and sensors [1]. Within this sphere, a number of bidentate boron-based systems have been reported, and the mode and strength of their interactions with a variety of anions investigated [2]. The possibility for stronger methide anion binding by a chelating receptor, for example, has led to the synthesis of a number of bifunctional Lewis acids (featuring various spacer groups) and to their investigation as potential alternatives to $B(C_6F_5)_3$ as olefin polymerization co-catalysts [2c,2d,2e,2f,2g,2h,2-l,2o]. By contrast, the geometric constraints imposed by a single atom spacer mean that systems of the type $X_2B\text{–}E'(R)_n\text{-}BX_2$ (E′ = first row element) are unlikely to bind a monodentate anion in chelating fashion [2d], being more appropriate to the complementary bidentate acid/base binding of anions, such as NO_3^-, AcO^- or $H_2PO_4^-$ [3].

Selective binding of bidentate anions such as carboxylates, RCO_2^- (and related anionic and neutral species such as dihydrogenphosphates, amino acids or aromatic nitro compounds) by hosts featuring an appropriate arrangement of hydrogen bond donors is of considerable relevance to biological systems [4]. Thus, for example, the binding properties of amides, ureas, thioureas and guanidinium derivatives which feature geometries appropriate for the complementary hydrogen bonding of such anions (**I**, Scheme 1), have been widely investigated [4]. Given the similarities in the spatial disposition of the binding sites in bifunctional boranes **II** and in hydrogen bond donors **I**, we were interested to investigate the possibility for the binding of bidentate anions by readily available bifunctional Lewis acids such as

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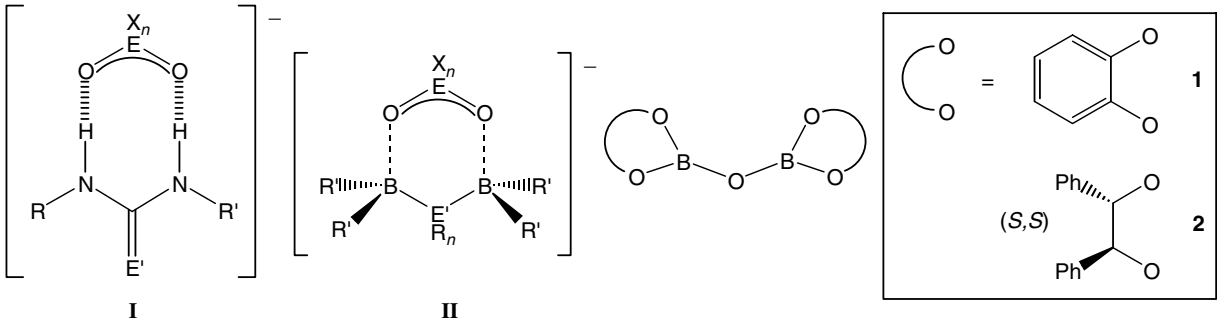


Scheme 1. Potential receptors for the binding of carboxylate and its isosteres using hydrogen bonding (**I**) or boron-based Lewis acids (**II**) such as **1** or **2**.

$(catB)_2O$ (**1**, cat = $O_2C_6H_4$-1,2) [5], along with analogous chiral receptors such as $(S,S\text{-}Ph_2C_2H_2O_2B)_2O$ (**2**).

2. Experimental

2.1. General

All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk line or dry box techniques unless otherwise stated. Solvents were pre-dried over sodium wire (hexanes, toluene) or molecular sieves (dichloromethane) and purged with nitrogen prior to distillation. Hexanes (potassium), toluene (sodium), and dichloromethane (calcium hydride) were then distilled from the appropriate drying agent before use. Chloroform-d and dichloromethane-d_2 (both Goss) were degassed and dried over molecular sieves prior to use. The compounds [PPN][OAc] [PPN = bis(triphenylphosphoranylidene)-ammonium, Ph_3PNPPh_3], [$^nBu_4N$][H_2PO_4], [$^nBu_4N$]F, B_2cat_2 (cat = catecholate, $O_2C_6H_4$-1,2) and $B(OH)_3$ were obtained from commercial sources and used as received. $(catB)_2O$ and *S*,*S*-$Ph_2C_2H_2(OH)_2$ were prepared by the literature routes [5,6].

NMR spectra were measured on a Bruker AM-400 or Jeol Eclipse 300 Plus FT-NMR spectrometer. Residual signals of solvent were used for reference for ^1H and ^{13}C NMR, while ^{11}B,^{19} F and ^{31} P NMR spectra were referenced with respect to $Et_2O \cdot BF_3$, $CFCl_3$ and 85% H_3PO_4, respectively. Infrared spectra were measured for each compound either as a solution in hexanes or pressed into a disk with an excess of dried KBr on a Nicolet 500 FT-IR spectrometer. Mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, University of Wales Swansea and by the departmental service. Perfluorotributylamine was used as the standard for high-resolution EI mass spectra. Elemental analyses were carried out both by the departmental service and by Warwick Analytical Service, University of Warwick.

Abbreviations: st = strong, md = medium, w = weak, s = singlet, d = doublet, t = triplet, q = quintet, sx = sextet, m = multiplet, br = broad.

2.2. Crystallographic method

Data were collected on an Enraf Nonius Kappa CCD diffractometer equipped with a Mo Kα radiation source (λ = 0.71073 Å). Data collection and cell refinement were carried out using DENZO [7], and structure solution and refinement (by full-matrix least-squares) using SIR-92, DIRDIFF-99 and SHELXL-97 [8–11], respectively. In each case, hydrogens were placed in idealised positions and refined using a riding model with U_{iso} set to 1.2 or 1.5 times the U_{eq} of the parent atom. Details of the data collection, structure solution and refinement for **4a**, and **5** can be found in Table 1; relevant bond lengths and angles are included in the figure captions. Complete details of all structures have been deposited with the CCDC and are included in the supporting information.

2.3. Syntheses

*Spectroscopic data for $(catB)_2O$ (**1**)*. Compound **1** was prepared by the previously reported route of Nöth and co-workers [5], and selected spectroscopic data are reported here merely for comparison of the 'free' receptor with subsequently derived anionic acid/base complexes. ^1H NMR (300 MHz, CD_2Cl_2) δ 7.13 (4H, m, aromatic CH), 7.24 (4H, m, aromatic CH). ^{11}B NMR (96 MHz, CD_2Cl_2) δ 21.5.

*Synthesis of $(S,S\text{-}Ph_2C_2H_2O_2B)_2O$ (**2**)*. Compound **2** was prepared from $B(OH)_3$ and *S*,*S*-$Ph_2C_2H_2(OH)_2$, by an analogous condensation route to that used for **1** [5,12]. Thus a mixture of $B(OH)_3$ (0.87 g, 1.41 mmol) and *S*,*S*-$Ph_2C_2H_2(OH)_2$ (3.01 g, 1.41 mmol) in toluene (150 cm^3) was heated at reflux for 72 h with azeotropic removal of water. Filtration, removal of volatiles in vacuo and recrystallization of the resulting off-white powder from dichloromethane/hexane at − 30 °C led to the isolation of **2** in yields of ca. 60% (2.01 g). ^1H NMR (300 MHz, CD_2Cl_2) δ 5.26 (4H, s, C*H*Ph), 7.27–7.37

Table 1
Crystallographic data for **4a** and **5**

	4a	**5**
Empirical formula	$C_{50}H_{41}B_2NO_7P_2$	$C_{64}H_{54}BNO_4P$
CCDC reference	253468	253469
Temperature (K)	150 (2)	150(2)
Formula weight	851.40	486.92
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	C2221
Unit cell dimensions		
a (Å)	15.0305(2)	11.8880(2)
b (Å)	17.8874(2)	17.5520(3)
c (Å)	15.9054(2)	24.2470(5)
α (°)	90	90
β (°)	94.7620(9)	90
γ (°)	90	90
Volume (Å3)	4261.51(9)	5059.34(16)
Z	4	8
Density (calc.) (Mg/m^3)	1.327	1.278
Absorption coefficient (mm^{-1})	0.158	0.138
F(000)	1776	2048
Crystal size (mm^3)	$0.35 \times 0.32 \times 0.25$	$0.25 \times 0.20 \times 0.20$
Theta range for data colln. (°)	2.95 to 27.50	3.26 to 27.48
Index ranges		
h	−19 to 19	−13 to 15
k	−23 to 23	−22 to 22
l	−20 to 20	−31 to 31
Reflections collected	78,830	20,796
Independent reflections, R_{int}	9791 (0.1065)	5558(0.0644)
Completeness to θ max. (%)	99.8	99.3
Absorption correction	DIFABS	Semi-empirical from equivalents
Max. and min. transmission	0.394, 0.128	0.9729, 0.9663
Data/restraints/parameters	9791/0/560	5558/0/326
Goodness-of-fit on F^2	1.028	1.052
Final *R* indices [$I > 2\sigma(I)$]		
R_1	0.0463	0.0456
wR_2	0.1054	0.0868
R indices (all data)		
R_1	0.0718	0.0707
wR_2	0.1173	0.0975
Absolute structure parameter	–	0.05(9)
Largest difference peak and hole (e $Å^{-3}$)	0.423, −0.423	0.246, −0.387

(20H, m, aromatic CH). ^{13}C NMR (76 MHz, CD_2Cl_2) δ 79.2 (*C*HPh), 125.9, 128.7, 128.9 (aromatic CH), 139.9 (aromatic quaternary). ^{11}B NMR (96 MHz, CD_2Cl_2) δ 21.7. IR (KBr, cm^{-1}) 2962 w, 1955 w, 1885 w, 1584 w, 1498 st, 1445 st, 1388 w, 1358 w, 1322 w, 1261 st, 1207 st, 1096 st, 1021 st. Mass spec (EI): *m/z* 462.2 [M^+, 100%]; exact mass: calc. 462.1804, meas. 462.1802.

*Interaction of **1** with bidentate anions*

(i) Reaction with [PPN][OAc]

To a solution of **1** (0.10 g, 0.39 mmol) in dichloromethane (5 cm^3) was added a solution containing 1 equiv. of [PPN][OAc] also in dichloromethane (5 cm^3). After stirring for 24 h, monitoring by ^{11}B NMR revealed complete conversion of **1** (δ_B 21.5) to a species giving rise to a single resonance at δ_B 13.4. Filtration, concentration (to ca. 3 cm^3) and layering with hexanes, led to the formation of [PPN][(catBOBcat) · (OAc)] (**4a**) as large colourless crystals suitable for X-ray crystallography (yield 0.25 g, 76%). ^1H NMR (300 MHz, $CDCl_3$) δ 2.09 (3H, s, CH_3 of OAc), 6.51 (4H, m, aromatic CH of cat), 6.61 (4H, m, aromatic CH of cat), 7.38–7.45 (24H, m, *ortho* and *meta* CHs of PPN), 7.60–7.65 (6H, m *para* CHs of PPN).^{13}C NMR (76 MHz, $CDCl_3$) δ 23.1 (CH_3 of AcO), 108.7, 117.4 (cat CHs), 127.0 (d, $^1J_{PC}$ = 108 Hz, PPN *ipso* C), 129.7, 132.1, 134.0 (PPN CHs), 152.2 (cat quaternary), 176.5 (AcO quaternary). ^{11}B NMR (96 MHz, $CDCl_3$) δ 13.4. ^{31} P NMR (121 MHz, $CDCl_3$) 21.7. IR (KBr, cm^{-1}) ν (OCO) 1577 st, 1460 md. Elemental analysis: calc. (for $C_{50}H_{41}B_2$ NO_7 P_2) C 70.54, N 1.64, H 4.85; meas. C 70.72, N 1.57, H 4.91. ^1H NMR titration experiments to determine the equilibrium constant for the binding of acetate to **1** were carried out by adding aliquots (typically 0.1 equiv. at a time) of **1** to 1 mmol of [PPN][OAc] in $CDCl_3$ (10.9 cm^3). The position of the resonance due to the acetate methyl group was monitored and data fitted using WinEQNMR (see Fig. 1) [13].

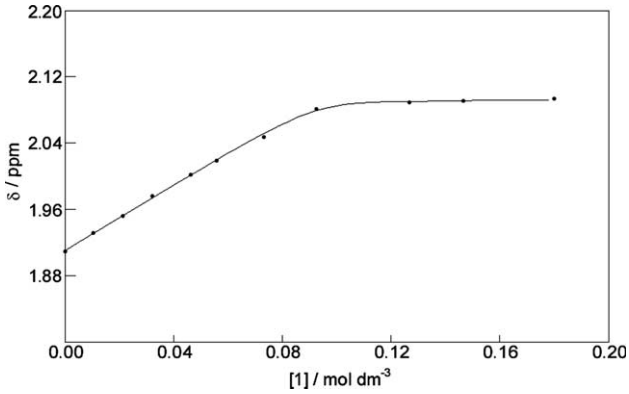


Fig. 1. ^1H NMR titration data for the addition of **1** to [PPN][OAc]. The curve was fitted to the experimental data points using WinEQNMR and gives a binding constant of 1500 ± 550 M^{-1} [13].

(ii) Reaction with [$^nBu_4N$][H_2PO_4]

To a solution of **1** (0.30 g, 1.18 mmol) in dichloromethane (5 cm^3) was added a solution containing 1 equiv. of [$^nBu_4N$][H_2PO_4] also in dichloromethane (5 cm^3). After stirring for 24 h, monitoring by ^{11}B NMR revealed complete conversion of **1** (δ_B 21.5) to a species giving rise to a single resonance at δ_B 13.1. Filtration, concentration (to ca. 3 cm^3) and layering with hexanes, led to the formation of [$^nBu_4N$][(catBOBcat) · (H_2PO_4)] (**4b**) as colourless crystals (yield 0.51 g, 73%). ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (12H, t, J = 7.3 Hz, CH_3 of ^{n}Bu), 1.28 (8H, virtual sx, J = 7.3 Hz, CH_2 of ^{n}Bu), 1.42 (8H, virtual q, J = 8.1 Hz, CH_2 of ^{n}Bu), 2.97 (8H, m, CH_2 of ^{n}Bu), 6.17 (2H, br s, OH of H_2PO_4), 6.59 (8H, m, aromatic CH of cat).^{13}C NMR (76 MHz, $CDCl_3$) δ 13.7 (CH_3 of ^{n}Bu), 19.6, 23.8, 57.9 (CH_2 s of ^{n}Bu), 108.7, 117.9 (aromatic CHs of cat), 151.8 (aromatic quaternary).

^{11}B NMR (96 MHz, $CDCl_3$) δ 13.1. ^{31}P NMR (121 MHz, $CDCl_3$) −21.5 (br). IR (KBr, cm^{-1}) ν(OPO)1234 md, 1097 md.

*Reaction of B_2cat_2 (**3**) with [PPN][OAc]*

To a solution of **3** (0.05 g, 0.21 mmol) in dichloromethane (5 cm^3) was added a solution containing 1 equiv. of commercial [PPN][OAc] (Aldrich) also in dichloromethane (5 cm^3). After stirring for 72 h, monitoring by ^{11}B NMR revealed complete conversion of **3** (δ_B 30.7) to a species giving rise to a single resonance at δ_B 13.4. Filtration, concentration (to ca. 1.5 cm^3) and layering with hexanes, led to the formation of large colourless crystals of **4a** having identical spectroscopic properties to samples prepared from **1**.

*Reaction of **2** with [PPN][OAc] – synthesis of [PPN][(S,S-$Ph_2C_2H_2O_2)_2B$] (**5**)*

To a solution of **2** (0.15 g, 0.32 mmol) in dichloromethane (5 cm^3) was added a solution containing 1 equiv. of [PPN][OAc] also in dichloromethane (5 cm^3). After stirring for 3 h, monitoring by ^{11}B NMR revealed complete consumption of **2** (δ_B 21.7) and the appearance of two new resonances at δ_B 19.6 and 10.6. Filtration, concentration (to ca. 2 cm^3) and layering with hexanes, led to the formation of [PPN][(*S*,*S*-$Ph_2C_2H_2O_2)_2B$] (**5**) as colourless crystals suitable for X-ray crystallography (yield 0.13 g, 42% based on boron, 84% based on chiral component). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.70 (4H, s, C*H*Ph), 7.02–7.60 (50H, m, aromatic CH of PPN and of CH*Ph*).^{13}C NMR (76 MHz, $CDCl_3$) δ 84.9 (*C*HPh), 125.7 (aromatic CH of anion), 127.0 (d, $^1J_{PC}$ = 108 Hz, PPN *ipso* C), 127.3, 127.4 (aromatic CHs of anion), 129.7, 132.1, 134.0 (PPN CHs), 139.9 (aromatic quaternary of anion). ^{11}B NMR (96 MHz, $CDCl_3$) δ 10.6. ^{31}P NMR (121 MHz, $CDCl_3$) 21.7. IR (KBr, cm^{-1}) 3154 w, 2962 w, 1815 w, 1793 w, 1646 w, 1560 w, 1439 st, 1381 st, 1261 st, 1094 st, 1016 md.

3. Results and discussion

Given significant recent interest in anion binding by boron-centred Lewis acids and in particular the development of bifunctional or chelating systems, we were interested in examining the anion binding properties of the pyroborate **1**. In addition, given that chiral Lewis acids offer the potential for enantioselective anion recognition and/or chiral delivery of achiral anions, we were interested in extending this investigation to homochiral receptors such as (*S*,*S*-$Ph_2C_2H_2O_2B)_2O$ (**2**). In practice, the chemistry reported by Nöth and co-workers for **1** [5] is readily extended to the synthesis of **2** from *S*,*S*-stilbenediol (Scheme 1), and **2** has been characterized by IR and multinuclear NMR spectroscopies and by mass spectrometry (including exact mass determination).

The interaction of **1** with one equivalent of acetate in chloroform solution is characterized by an upfield shift in the ^{11}B NMR resonance (δ_B 21.5–13.1) and by a downfield shift (δ_H 1.91–2.09) in the acetate CH_3 ^{1}H NMR signal. The former shift is characteristic of quaternization of the boron centre on anion binding [14], and is consistent with a symmetrically bound η^2(O,O) acetate ligand, or with rapidly fluxional η^1 coordination. Proton NMR titration measurements (Fig. 1) are consistent with a 1:1 binding stoichiometry, and yield a binding constant of 1500 ± 550 M^{-1}. This value is similar to that determined for the binding of carboxylate anions to simple urea-based receptors in chloroform solution (e.g., 1300 ± 200 M^{-1} [4d]), but about one order of magnitude less than those reported, for example, by Beer and by Smith for the binding of AcO^- to receptors featuring either macrocyclic or Lewis acid assisted binding domains [4f,4g,4h]. Our results are also indicative of a significantly stronger acetate/Lewis acid interaction than has been reported for boronate ester systems of the type ArBpin (pin = $OCMe_2CMe_2O$). Based on ^{11}B NMR data, such systems have been reported to show 'no affinity' for acetate [4f].

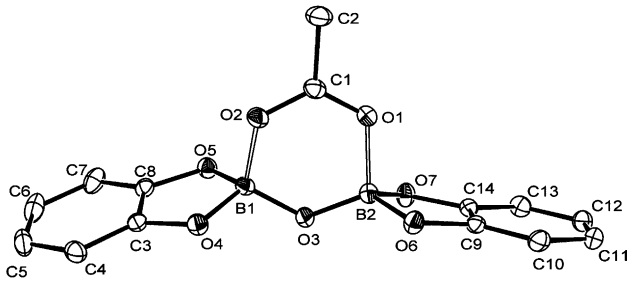


Fig. 2. Structure of the anionic component of [PPN][(catBOBcat) · (OAc)], **4a**; hydrogen atoms omitted for clarity. Important bond lengths (Å) and angles (°): B(1)–O(2) 1.574(2), O(2)–C(1) 1.265(2), C(1)–O(1) 1.265(2), O(1)–B(2) 1.617(3), B(2)–O(3) 1.375(2), O(3)–B(1) 1.393(2), B(1)–O(4) 1.470(2), O(1)–C(1)–O(2) 124.15(17), B(1)–O(3)–B(2) 128.90(16), O(3)–B(1)–O(4) 114.46(16), O(3)–B(1)–O(5) 115.15(16), O(4)–B(1)–O(5) 105.59(15).

The preceding spectroscopic inferences were given further credence by the results of an X-ray diffraction study undertaken on crystals obtained by diffusion of hexane into a dichloromethane solution. The structure of the adduct $[(catBOBcat) \cdot (OAc)]^-$ (**4a**) so obtained (as the PPN salt, Fig. 2 and Table 1) confirms its 1:1 stoichiometry and the complementary nature of the bidentate anion/bidentate Lewis acid interaction. This mode of binding and the six-membered chelate ring so formed are similar to those observed by Uhl and co-workers [3,15] for the adduct $[(R_2AlCH_2AlR_2) \cdot (NO_3)]^-$ [R = $CH(SiMe_3)_2$]; a similar structural motif is also found in a number of neutral boron-containing species. In the case of **4a** there is noticeable puckering of the six-membered ring due to the fact that the CO_2 unit of the acetate 'ligand' and the BOB bridge of the Lewis acid chelate are not co-planar. Thus the C(1)–O(2)–B(1)–

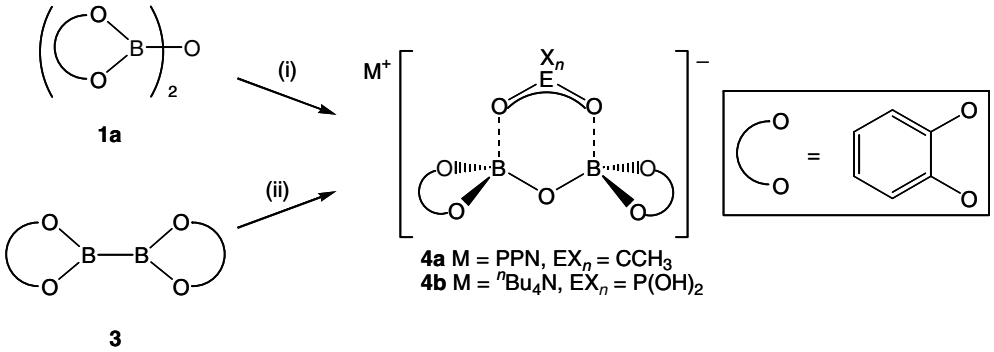
O(3) and C(1)–O(1)–B(2)–O(3) torsion angles are 20.9(2) and 17.5(2)°, respectively. Further asymmetry within the chelate ring reflects small but significant differences in the binding of the two acetate oxygen donors; thus, disparate B–O(acetate) distances of 1.574(2) and 1.617(3) Å are observed, presumably reflecting a marginally stronger O(2)–B(1) interaction [over O(1)–B(2)] in the solid state. Consistent with this, the lengthening of the B(1)–O(3) bond [1.393(2) Å] with respect to that observed in the free $(catB)_2O$ receptor [1.346(2) Å] is significantly greater than that found for B(2)–O(3) [1.375(2) Å] [5]. Further structural differences between the acetate complex **4a** and the free receptor **1** include the increased B–O bond lengths and decreased OBO angles at the boron centre expected on quaternization. Interestingly, the increased bond lengths for the B–O–B fragment found in the complex **4a** are almost entirely offset by a narrowing of the B–O–B angle [128.90(16) Å for **4a**, 135.9(2) for **1**], such that the B···B separation is essentially unchanged [2.498(2) and 2.495 Å, respectively] [5]. This observation implies a near ideal interboron separation in the B–O–B unit of **1** with respect to the complementary binding of acetate.

Interestingly complex **4a** is also the product isolated from the reaction of B_2cat_2 with one equivalent of commercial (i.e., wet) [PPN][OAc]. At short reaction times, ^{11}B monitoring is consistent with fluxional η^1 binding of AcO^- to B_2cat_2 [16], but after 72 h the predominant product is **4a**, possibly formed by insertion of a water-derived oxygen atom into the B–B bond of **3**. Such a reaction presumably reflects the thermodynamic stability of the complementary AcO^- binding in **4a**, and in turn the better match of acetate O···O separation (2.236 Å in **4a**) to the B···B separation in **1** (2.495 Å vs. 1.678 Å in B_2cat_2 [17]).

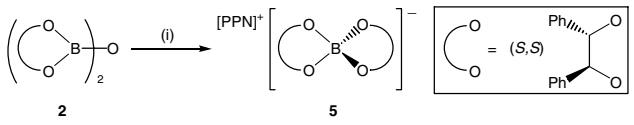
^1H and ^{11}B NMR data obtained from isolated crystalline samples of **4a** are identical to those obtained for in situ acetate binding experiments. In addition, IR measurements for both isolated crystalline samples of **4a** and for the adduct in dichloromethane solution are consistent with the crystallographically determined structure. Thus, acetate OCO stretching vibrations at 1577 (ν_{as}) and 1460 cm^{-1} (ν_s) are consistent with previously reported examples of this type of coordination (c.f. values of 1588, 1426 and 1585, 1428 cm^{-1} for acetate ligands bridging dinickel and dizinc systems, respectively [18]). Similar analyses of the spectroscopic data obtained for the species formed on exposure of **1** to $[H_2PO_4]^-$ or to F^- allow some comments to be made concerning the structures of these adducts. Thus the ^{11}B resonance for **4b**, the 1:1 adduct isolated from **1** and $[H_2PO_4]^-$, has a very similar chemical shift (δ_B 13.1) to that for observed for **4a**, and does not vary significantly with temperature. Furthermore, OPO stretching vibrations at 1234 and 1097 cm^{-1} are similar to values of 1200 and 1130 cm^{-1} for previously reported examples of η^2(O,O) bound $[H_2PO_4]^-$ ligands [18]. Although single crystals suitable for X-ray diffraction were not forthcoming a structure analogous to **4a** is therefore conceivable for the complex $[(catBOBcat)\cdot(H_2PO_4)]^-$ (Scheme 2).

Not unexpectedly, given the constraints of B–O–B bridge, the interaction **1** with one equivalent of fluoride in chloroform solution appears to involve binding to a single boron centre and fluoride exchange between the two Lewis acidic sites. Hence at room temperature, two broad overlapping ^{11}B resonances are observed which coalesce at 50° to a single signal (δ_B 18.0), and which can be resolved into two distinct signals at −20 °C. The positions of the latter two resonances (δ_B 13.8 and 21.0) are consistent, respectively, with a four-coordinate fluoride-complexed boron and a vacant three-coordinate site.

Given that pyroborate **1** has been shown to act as a chelating Lewis acid in the complementary binding of acetate and dihydrogen phosphate, we were interested to determine whether similar binding properties for homochiral analogue **2** might be exploited in the enantioselective recognition (or delivery) of carboxylate or phosphate derived anions [19]. In the event, the reaction



Scheme 2. Complementary binding of bifunctional Lewis bases by pyroborate **1a**. Conditions: (i) [M][X_n E(=O)O] (1 equiv.), dichloromethane, 20 °C, 24 h, 76%; (ii) commercial [PPN][OAc] (1 equiv.), dichloromethane, 20 °C, 96 h, 68%.



2 5

Scheme 3. Reaction of pyroborate **2** with [PPN][OAc] – synthesis of homo-chiral borate anion [(*S*,*S*-$Ph_2C_2H_2O_2)_2B$] (**5**). Conditions: (i) [PPN][OAc] (1 equiv.), dichloromethane, 20 °C, 3 h, 84% (based on chiral component).

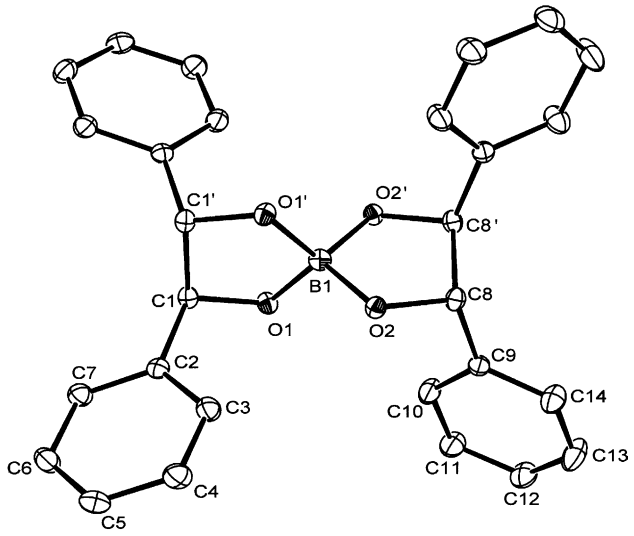


Fig. 3. Structure of the anionic component of [PPN][(*S*,*S*-$Ph_2C_2H_2O_2)_2B$], **5**; hydrogen atoms omitted for clarity. Important bond lengths (Å) and angles (°): B(1)–O(1) 1.473(3), B(1)–O(2) 1.482(3), O(1)–C(1) 1.412(3), C(1)–C(1′) 1.564(4), O(1)–B(1)–O(2) 115.82(8), O(1)–B(1)–O(1′) 104.2(3).

of **2** with a single equivalent of [PPN][OAc] leads not to the analogous 1:1 adduct, but to the homochiral borate anion [(*S*,*S*-$Ph_2C_2H_2O_2)_2B]^-$, as the $[PPN]^+$ salt (**5**, Scheme 3). The empirical formula of **5** was implied by multinuclear NMR, and subsequently confirmed crystallographically (Fig. 3). The overall yield of **5** from this reaction (84% based on incorporation of the chiral component, 42% based on boron) represents a high yielding, simple synthesis of a homochiral borate anion [20].

4. Conclusions

The pyroborate $(catB)_2O$ (**1**) has been shown to act as a bifunctional Lewis acid, exemplified by the complementary (1:1) binding of acetate in solid state (as demonstrated crystallographically). A similar structure is implied in solution by spectroscopic data and a binding constant of 1500–550 M^{-1} determined by proton titration techniques. By contrast, the reaction of (*S*,*S*-$Ph_2C_2H_2O_2B)_2O$ (**2**) with acetate leads to breakdown of the Lewis acid chelate and to the formation of the homochiral borate anion [(*S*,*S*-$Ph_2C_2H_2O_2)_2B]^-$.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.01.015.

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