

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1242). Services for accessing these data are described at the back of the journal.

## References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
- Ellison, J. J., Ruhlandt-Senge, K., Hope, H. & Power, P. P. (1995). *Inorg. Chem.* **34**, 49–55.
- Kienitz, C. O., Thöne, C. & Jones, P. G. (1996). *Inorg. Chem.* **35**, 3990–3997.
- Mont, W.-W. du, Martens, A., Pohl, S. & Saak, W. (1990). *Inorg. Chem.* **29**, 4847–4848.
- Nicolet (1987a). *P3 Software*. Nicolet Analytical X-ray Instruments, Madison, Wisconsin, USA.
- Nicolet (1987b). *XDISK*. Nicolet Analytical X-ray Instruments, Madison, Wisconsin, USA.
- Ostrowski, M., Jeske, J., Jones, P. G. & du Mont, W.-W. (1993). *Chem. Ber.* **126**, 1355–1359.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1994a). *XEMP. Empirical Absorption Program*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1994b). *XP. Molecular Graphics Program*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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## Salts of the Bis(catecholato)borate Anion with Organic Cations

WILLIAM CLEGG,<sup>a</sup> ANDREW J. SCOTT,<sup>a</sup> FIONA J. LAWLOR,<sup>b</sup> NICHOLAS C. NORMAN,<sup>b</sup> TODD B. MARDER,<sup>c</sup> CHAOYANG DAI<sup>d</sup> AND PAUL NGUYEN<sup>d</sup>

<sup>a</sup>Department of Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, England, <sup>b</sup>School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, England, <sup>c</sup>Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England, and <sup>d</sup>Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1. E-mail: w.clegg@ncl.ac.uk

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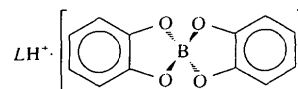
### Abstract

In a series of six salts with organic nitrogen and phosphorus cations [2-methylpyridinium bis(pyrocatecholato-*O,O'*)borate,  $C_6H_8N^+ \cdot C_{12}H_8BO_4^-$ , (1); 4-methylpyridinium bis(pyrocatecholato-*O,O'*)borate,  $C_6H_8N^+ \cdot C_{12}H_8BO_4^-$ , (2) and (3) (two polymorphs); 1,10-phenanthrolium bis(pyrocatecholato-*O,O'*)borate,

$C_{12}H_9N_2^+ \cdot C_{12}H_8BO_4^-$ , (4), and its dichloromethane solvate,  $C_{12}H_9N_2^+ \cdot C_{12}H_8BO_4^- \cdot CH_2Cl_2$ , (5); and trimethylphosphonium bis(pyrocatecholato-*O,O'*)borate,  $C_3H_{10}P^+ \cdot C_{12}H_8BO_4^-$ , (6)], the bis(catecholato)borate anion has approximate  $D_{2d}$  ( $\bar{4}2m$ ) symmetry, with the central spiro-B atom distorted from regular tetrahedral coordination geometry by reduction of the two intraring O—B—O bond angles. The two chelate rings show small deviations from planarity by folding about the O···O axis. Ion pairs are formed by N—H···O hydrogen bonding in all five salts with nitrogen-based cations, but there is no hydrogen bonding in the phosphonium salt; the hydrogen bonding leads to slight elongation of the B—O bond involved.

### Comment

We report the structures of a series of salts of the bis(catecholato)borate [bis(benzene-1,2-diolato)borate] anion with organic nitrogen and phosphorus cations. These have been obtained as side products in the study of the reactions of diboron compounds with organic bases to produce Lewis acid–base adducts. The formation of the bis(catecholato)borate anion seems to be favoured under a wide variety of conditions. Traces of moisture are probably responsible for the reactions leading to these products.



- (1)  $L = 2\text{-MeC}_5\text{H}_4\text{N}$   
 (2),(3)  $L = 4\text{-MeC}_5\text{H}_4\text{N}$   
 (4),(5)  $L = 1,10\text{-phenanthroline}$   
 (6)  $L = \text{Me}_3\text{P}$

The specific compounds reported here contain the cations 2-methylpyridinium, (1), 4-methylpyridinium, (2) and (3), 1,10-phenanthrolium, (4) and (5), and trimethylphosphonium, (6).

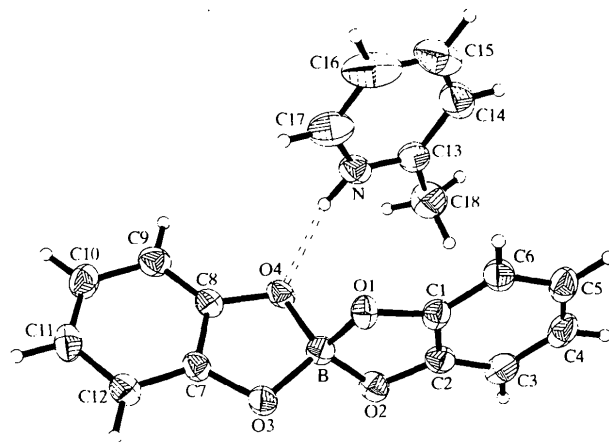


Fig. 1. The molecular structure of (1), with atom labels and 50% probability ellipsoids for non-H atoms.

Structures (2) and (3) are polymorphs of the same chemical compound, and compound (1) has an isomer of the same cation with a 2-methyl in place of the 4-methyl substituent. Compounds (4) and (5) have the same ions, but (4) is unsolvated and (5) is a dichloromethane solvate. Compound (6) is the only phosphonium salt in what is otherwise a series of salts with protonated pyridine and 1,10-phenanthroline cations, and it has two cations and two anions in the asymmetric unit.

Except for a small effect caused by hydrogen bonding (see below), the geometry of the  $[B(cat)_2]^-$  anion (cat = catecholato) is essentially the same in all six structures, and the same as observed previously in other salts of the same anion with a variety of organic and inorganic

cations (Clegg *et al.*, 1998; Goddard *et al.*, 1993; Graf, Hosseini, Ruppert, De Cian & Fischer, 1995; Graf, Hosseini, Ruppert, Kyritsakas *et al.*, 1995; Graf *et al.*, 1996; Griffith *et al.*, 1996; He & Hartwig, 1996; Mohr *et al.*, 1990; Westcott *et al.*, 1991, 1993). The B atom has a slightly distorted tetrahedral coordination geometry, with the two smallest O—B—O angles within the two chelate rings being several degrees smaller than the other four angles. The chelate rings are close

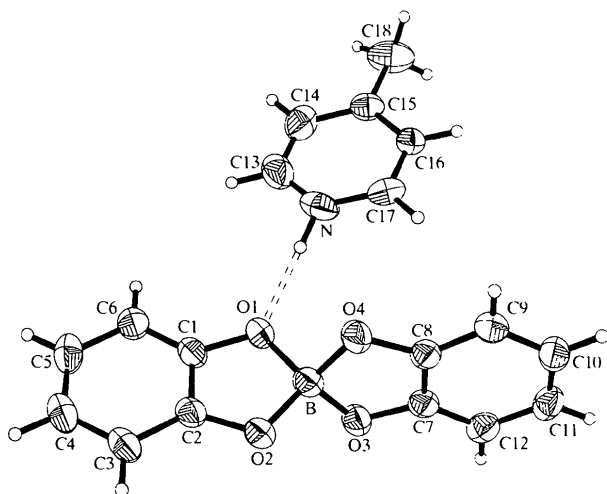


Fig. 2. The molecular structure of (2), with atom labels and 50% probability ellipsoids for non-H atoms.

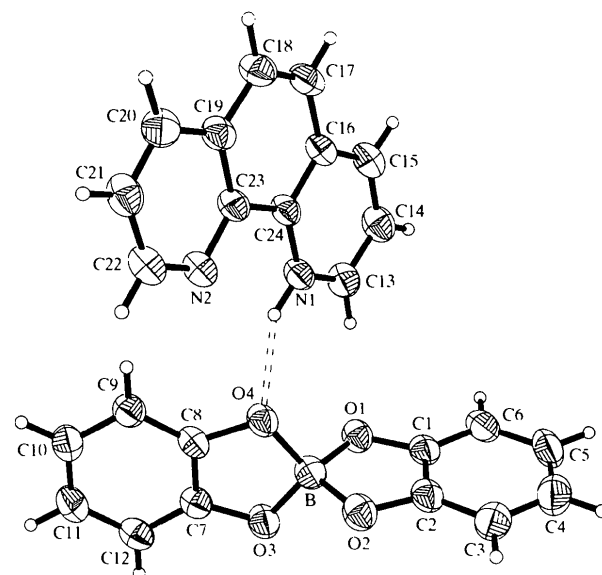


Fig. 4. The molecular structure of (4), with atom labels and 50% probability ellipsoids for non-H atoms.

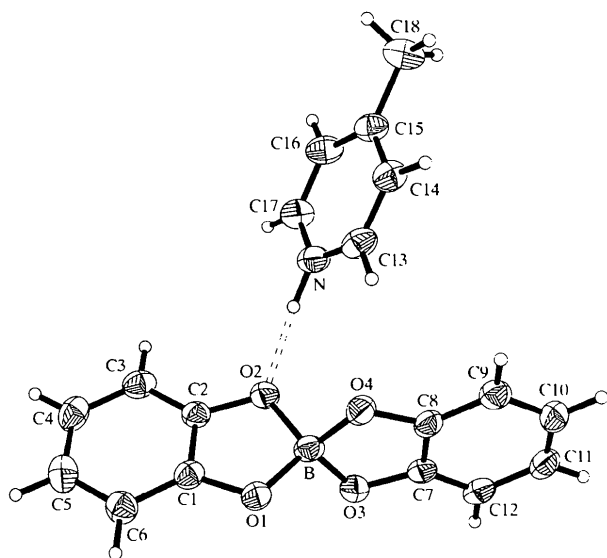


Fig. 3. The molecular structure of (3), with atom labels and 50% probability ellipsoids for non-H atoms.

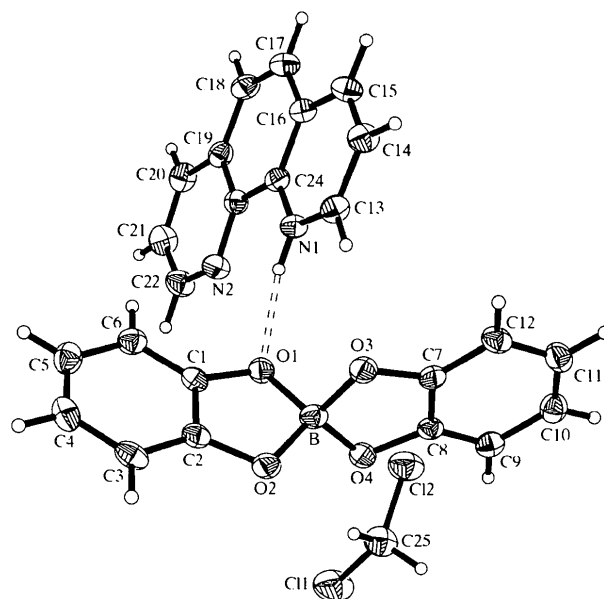


Fig. 5. The molecular structure of (5), with atom labels and 50% probability ellipsoids for non-H atoms.

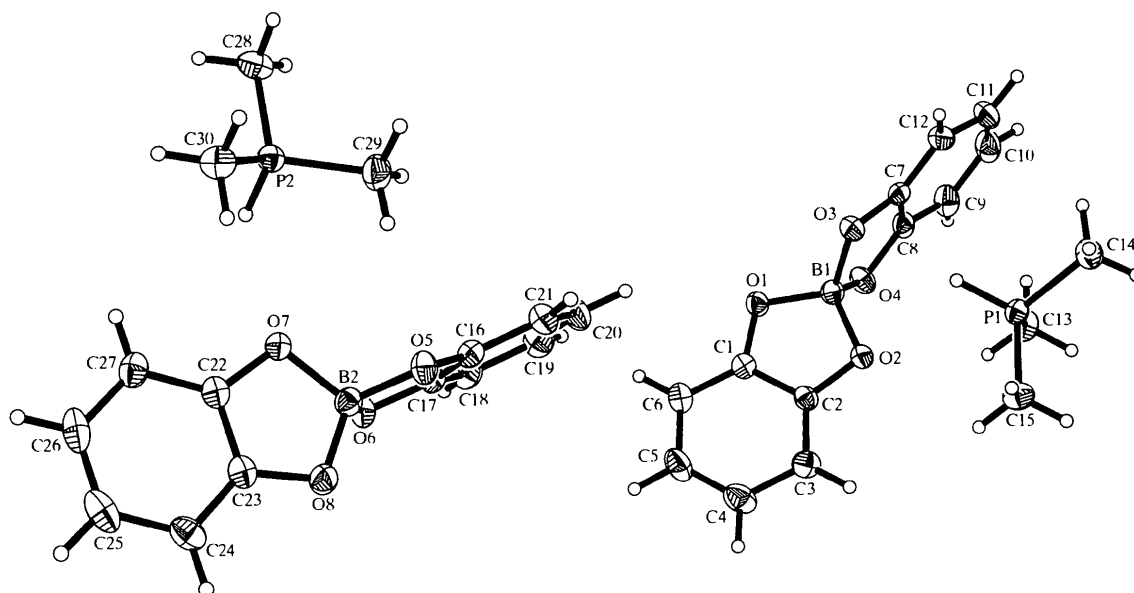


Fig. 6. The molecular structure of (6), with atom labels and 50% probability ellipsoids for non-H atoms.

to planar, with r.m.s. deviations up to a maximum of 0.055 Å; a slight folding about the O···O axis, with a dihedral angle in the range 0.8(2)–13.9(2)° between BO<sub>2</sub> and O<sub>2</sub>C<sub>2</sub> planes (which all have r.m.s. deviations below 0.007 Å), sets B as the flap atom of an envelope and is presumably due to variations in crystal packing forces in the different structures. The two chelate rings are perpendicular within 3° in all cases, giving an approximate *D*<sub>2d</sub> (*42m*) point-group symmetry for the anion.

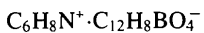
In all the structures (1)–(5), with cations which are protonated aromatic nitrogen bases, the N—H bond of the cation is hydrogen bonded to one of the O atoms of the anion. These hydrogen bonds are shown dashed in Figs. 1–5, and the hydrogen-bond geometry is summarized in Table 7. The position of the H atom involved was refined freely in each case. In every one of the five structures, the hydrogen-bonded O atom forms the longest B—O bond. This is a consistent pattern, although some of the differences are very small and, individually, not statistically significant. A similar slight lengthening of the B—O bond has been observed in other [B(cat)<sub>2</sub>]<sup>−</sup> anions where hydrogen bonding occurs, or in which one or more O atoms are involved in coordination to a metal centre (Clegg *et al.*, 1998; Goddard *et al.*, 1993; Graf, Hosseini, Ruppert, De Cian & Fischer, 1995; Graf, Hosseini, Ruppert, Kyritsakas *et al.*, 1995; Graf *et al.*, 1996; Griffith *et al.*, 1996; He & Hartwig, 1996). Any lengthening of the corresponding C—O bond is very small, and no effect on the B—O—C angle is discernible. The hydrogen bonding in these five structures generates individual ion pairs.

There is no hydrogen bonding in the phosphonium salt, (6), for which the P—H H-atom positions were

also refined freely, and in which the H···O distances are all greater than 2.45 Å.

## Experimental

All the compounds were obtained as side products in reactions designed to form adducts of B<sub>2</sub>(cat)<sub>2</sub> or B<sub>2</sub>(cat)<sub>3</sub> with Lewis bases. Analytical and spectroscopic data have not been obtained. In a typical synthesis of (1), equimolar quantities (0.3 mmol) of B<sub>2</sub>(cat)<sub>3</sub> and 2-picoline were dissolved in toluene and mixed. Small quantities of (1) were obtained as single crystals from this solution on standing. The synthesis of (2) and (3) depends on the reaction between B<sub>2</sub>(cat)<sub>2</sub> and 4-picoline, which has been described by Nguyen *et al.* (1995). Addition of one or two molar equivalents of 4-picoline to B<sub>2</sub>(cat)<sub>2</sub> (typically 5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub> gives a colourless solution. Slow diffusion of an overlayer of *n*-hexane affords either B<sub>2</sub>(cat)<sub>2</sub>(4-picoline) or B<sub>2</sub>(cat)<sub>2</sub>(4-picoline)<sub>2</sub> as the major crystalline product, with variable small amounts of compound (2) or (3) as a side product. In a typical reaction to synthesize (4), 1,10-phenanthroline (57 mg, 0.31 mmol) in toluene (1 ml) was added to B<sub>2</sub>(cat)<sub>3</sub> (100 mg, 0.28 mmol) in toluene (3 ml). A yellow precipitate formed immediately. The reaction mixture was stirred for 30 min and then filtered. The precipitate was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> to give compound (4). Compound (5) was formed from B<sub>2</sub>(cat)<sub>2</sub> and one equivalent of 1,10-phenanthroline in an analogous reaction to that for compounds (2) and (3) (Dai *et al.*, 1998). The major product is B<sub>2</sub>(cat)<sub>2</sub>(phen); small quantities of (5) were obtained by recrystallization of the reaction mixture from a mixed CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane solvent by diffusion. In a typical synthesis of (6), B<sub>2</sub>(cat)<sub>3</sub> (100 mg, 0.29 mmol) was dissolved in CDCl<sub>3</sub> (1 ml), and PMe<sub>3</sub> (44 mg, 0.58 mmol) was added. The solution turned cloudy, then cleared. A small number of colourless crystals formed after about 2 h, and these were separated.

**Compound (1)***Crystal data* $M_r = 321.13$ 

Monoclinic

Cc

 $a = 7.5204 (10) \text{ \AA}$  $b = 17.061 (2) \text{ \AA}$  $c = 12.2921 (17) \text{ \AA}$  $\beta = 92.187 (4)^\circ$  $V = 1576.0 (4) \text{ \AA}^3$  $Z = 4$  $D_x = 1.353 \text{ Mg m}^{-3}$  $D_m$  not measured*Data collection*

Bruker SMART CCD

diffractometer

 $\omega$  rotation with narrow

frames

Absorption correction: none

4758 measured reflections

2468 independent reflections

*Refinement*Refinement on  $F^2$  $R[F^2 > 2\sigma(F^2)] = 0.044$  $wR(F^2) = 0.111$  $S = 1.088$ 

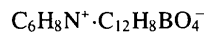
2468 reflections

218 parameters

H atoms: see below

 $w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 1.7798P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.004$  $\Delta\rho_{\max} = 0.390 \text{ e \AA}^{-3}$  $\Delta\rho_{\min} = -0.308 \text{ e \AA}^{-3}$ Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (1)

B—O3	1.463 (4)	B—O1	1.493 (3)
B—O2	1.470 (4)	B—O4	1.519 (3)
O3—B—O2	114.2 (2)	O3—B—O4	104.7 (2)
O3—B—O1	113.1 (2)	O2—B—O4	111.4 (2)
O2—B—O1	105.1 (2)	O1—B—O4	108.3 (2)

**Compound (2)***Crystal data* $M_r = 321.13$ 

Monoclinic

 $P2_1/n$  $a = 11.6469 (14) \text{ \AA}$  $b = 10.9779 (14) \text{ \AA}$  $c = 13.5215 (17) \text{ \AA}$  $\beta = 112.482 (3)^\circ$  $V = 1597.4 (3) \text{ \AA}^3$  $Z = 4$  $D_x = 1.335 \text{ Mg m}^{-3}$  $D_m$  not measuredMo  $K\alpha$  radiation $\lambda = 0.71073 \text{ \AA}$ 

Cell parameters from 3393

reflections

 $\theta = 2.39\text{--}28.23^\circ$  $\mu = 0.095 \text{ mm}^{-1}$  $T = 160 (2) \text{ K}$ 

Block

 $0.34 \times 0.20 \times 0.14 \text{ mm}$ 

Colourless

2277 reflections with

 $I > 2\sigma(I)$  $R_{\text{int}} = 0.027$  $\theta_{\max} = 28.37^\circ$  $h = -9 \rightarrow 9$  $k = -18 \rightarrow 21$  $l = -12 \rightarrow 16$ 

Intensity decay: none

Extinction correction:

*SHELXTL* (Sheldrick, 1994)

Extinction coefficient:

0.0040 (7)

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Absolute structure:

Flack (1983)

Flack parameter =  $-1.4 (13)$ *Data collection*

Bruker SMART CCD

diffractometer

 $\omega$  rotation with narrow

frames

Absorption correction: none

9521 measured reflections

3579 independent reflections

*Refinement*Refinement on  $F^2$  $R[F^2 > 2\sigma(F^2)] = 0.043$  $wR(F^2) = 0.109$  $S = 1.027$ 

3579 reflections

223 parameters

H atoms: see below

 $w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 0.4846P]$ where  $P = (F_o^2 + 2F_c^2)/3$ 

2567 reflections with

 $I > 2\sigma(I)$  $R_{\text{int}} = 0.037$  $\theta_{\max} = 28.26^\circ$  $h = -15 \rightarrow 14$  $k = -13 \rightarrow 14$  $l = -7 \rightarrow 17$ 

Intensity decay: none

 $(\Delta/\sigma)_{\max} = 0.001$  $\Delta\rho_{\max} = 0.209 \text{ e \AA}^{-3}$  $\Delta\rho_{\min} = -0.158 \text{ e \AA}^{-3}$ 

Extinction correction:

*SHELXTL*

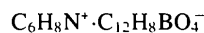
Extinction coefficient:

0.0083 (10)

Scattering factors from

*International Tables for Crystallography* (Vol. C)Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (2)

B—O2	1.474 (2)	B—O4	1.487 (2)
B—O3	1.483 (2)	B—O1	1.490 (2)
O2—B—O3	112.46 (13)	O2—B—O1	104.68 (13)
O2—B—O4	113.35 (14)	O3—B—O1	112.64 (14)
O3—B—O4	104.84 (13)	O4—B—O1	109.01 (13)

**Compound (3)***Crystal data* $M_r = 321.13$ 

Monoclinic

 $P2_1/n$  $a = 9.944 (3) \text{ \AA}$  $b = 11.116 (3) \text{ \AA}$  $c = 14.491 (4) \text{ \AA}$  $\beta = 94.900 (15)^\circ$  $V = 1595.9 (8) \text{ \AA}^3$  $Z = 4$  $D_x = 1.337 \text{ Mg m}^{-3}$  $D_m$  not measuredMo  $K\alpha$  radiation $\lambda = 0.71073 \text{ \AA}$ 

Cell parameters from 98

reflections

 $\theta = 1.0\text{--}23.5^\circ$  $\mu = 0.094 \text{ mm}^{-1}$  $T = 160 (2) \text{ K}$ 

Block

 $0.40 \times 0.32 \times 0.26 \text{ mm}$ 

Colourless

*Data collection*

Bruker SMART CCD

diffractometer

 $\omega$  rotation with narrow

frames

Absorption correction: none

4469 measured reflections

3204 independent reflections

2300 reflections with

 $I > 2\sigma(I)$  $R_{\text{int}} = 0.029$  $\theta_{\max} = 28.40^\circ$  $h = -13 \rightarrow 10$  $k = -14 \rightarrow 13$  $l = -6 \rightarrow 19$ 

Intensity decay: none

*Refinement*Refinement on  $F^2$  $R[F^2 > 2\sigma(F^2)] = 0.042$  $wR(F^2) = 0.103$  $(\Delta/\sigma)_{\max} < 0.001$  $\Delta\rho_{\max} = 0.194 \text{ e \AA}^{-3}$  $\Delta\rho_{\min} = -0.154 \text{ e \AA}^{-3}$

$S = 1.051$   
 3204 reflections  
 223 parameters  
 H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.0411P)^2 + 0.3942P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

Extinction correction:  
*SHELXTL*  
 Extinction coefficient:  
 0.0092 (12)  
 Scattering factors from  
*International Tables for Crystallography* (Vol. C)

**Compound (5)**

*Crystal data*  
 $C_{12}H_9N_2^+ \cdot C_{12}H_8BO_4^- \cdot CH_2Cl_2$   
 $M_r = 493.13$   
 Triclinic  
 $P\bar{1}$   
 $a = 10.3594$  (11) Å  
 $b = 11.0153$  (11) Å  
 $c = 12.0742$  (13) Å  
 $\alpha = 96.361$  (2)°  
 $\beta = 107.932$  (2)°  
 $\gamma = 115.848$  (2)°  
 $V = 1130.4$  (2) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 1.449$  Mg m<sup>-3</sup>  
 $D_m$  not measured

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073$  Å  
 Cell parameters from 3565 reflections  
 $\theta = 2.14$ – $26.27$ °  
 $\mu = 0.324$  mm<sup>-1</sup>  
 $T = 160$  (2) K  
 Block  
 $0.18 \times 0.14 \times 0.10$  mm  
 Orange

Table 3. Selected geometric parameters (Å, °) for (3)

B—O1	1.465 (2)	B—O4	1.479 (2)
B—O3	1.478 (2)	B—O2	1.505 (2)
O1—B—O3	112.66 (14)	O1—B—O2	104.55 (14)
O1—B—O4	113.41 (15)	O3—B—O2	112.07 (15)
O3—B—O4	104.99 (14)	O4—B—O2	109.30 (13)

**Compound (4)***Crystal data*

$C_{12}H_9N_2^+ \cdot C_{12}H_8BO_4^-$   
 $M_r = 408.21$   
 Orthorhombic  
*Pbcn*  
 $a = 16.120$  (2) Å  
 $b = 15.959$  (2) Å  
 $c = 14.9294$  (19) Å  
 $V = 3840.7$  (9) Å<sup>3</sup>  
 $Z = 8$   
 $D_x = 1.412$  Mg m<sup>-3</sup>  
 $D_m$  not measured

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073$  Å  
 Cell parameters from 9723 reflections  
 $\theta = 1.79$ – $27.64$ °  
 $\mu = 0.096$  mm<sup>-1</sup>  
 $T = 160$  (2) K  
 Block  
 $0.28 \times 0.24 \times 0.18$  mm  
 Yellow

*Data collection*

Bruker SMART CCD diffractometer  
 $\omega$  rotation with narrow frames  
 Absorption correction: none  
 22 321 measured reflections  
 4515 independent reflections

2743 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.051$   
 $\theta_{max} = 28.43$ °  
 $h = -20 \rightarrow 20$   
 $k = -21 \rightarrow 20$   
 $l = -12 \rightarrow 19$   
 Intensity decay: none

*Refinement*

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.055$   
 $wR(F^2) = 0.177$   
 $S = 1.025$   
 4515 reflections  
 285 parameters  
 H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.1076P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.329$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.253$  e Å<sup>-3</sup>  
 Extinction correction:  
*SHELXTL*  
 Extinction coefficient:  
 0.0033 (7)

Scattering factors from  
*International Tables for Crystallography* (Vol. C)

*Data collection*

Bruker SMART CCD diffractometer  
 $\omega$  rotation with narrow frames  
 Absorption correction: none  
 6167 measured reflections  
 4331 independent reflections

3501 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.035$   
 $\theta_{max} = 26.37$ °  
 $h = -12 \rightarrow 12$   
 $k = -13 \rightarrow 13$   
 $l = -13 \rightarrow 14$   
 Intensity decay: none

*Refinement*

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.043$   
 $wR(F^2) = 0.100$   
 $S = 1.095$   
 4331 reflections  
 312 parameters  
 H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.0166P)^2 + 0.9928P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.249$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.457$  e Å<sup>-3</sup>  
 Extinction correction:  
*SHELXTL*  
 Extinction coefficient:  
 0.0051 (9)  
 Scattering factors from  
*International Tables for Crystallography* (Vol. C)

Table 5. Selected geometric parameters (Å, °) for (5)

B—O4	1.472 (3)	B—O3	1.487 (3)
B—O2	1.473 (3)	B—O1	1.501 (3)
O4—B—O2	113.75 (17)	O4—B—O1	112.16 (17)
O4—B—O3	105.32 (17)	O2—B—O1	104.50 (17)
O2—B—O3	110.88 (17)	O3—B—O1	110.34 (17)

**Compound (6)***Crystal data*

$C_3H_{10}P^+ \cdot C_{12}H_8BO_4^-$   
 $M_r = 304.07$   
 Monoclinic  
 $P2_1/c$   
 $a = 22.417$  (3) Å  
 $b = 8.4390$  (9) Å  
 $c = 17.4208$  (19) Å  
 $\beta = 110.477$  (3)°  
 $V = 3087.4$  (6) Å<sup>3</sup>  
 $Z = 8$   
 $D_x = 1.308$  Mg m<sup>-3</sup>  
 $D_m$  not measured

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073$  Å  
 Cell parameters from 8289 reflections  
 $\theta = 1.94$ – $28.09$ °  
 $\mu = 0.189$  mm<sup>-1</sup>  
 $T = 160$  (2) K  
 Block  
 $0.16 \times 0.14 \times 0.14$  mm  
 Colourless

Table 4. Selected geometric parameters (Å, °) for (4)

B—O3	1.466 (3)	B—O1	1.486 (2)
B—O2	1.484 (3)	B—O4	1.488 (2)
O3—B—O2	110.96 (17)	O3—B—O4	105.42 (15)
O3—B—O1	112.52 (16)	O2—B—O4	113.03 (16)
O2—B—O1	104.76 (15)	O1—B—O4	110.32 (16)

**Data collection**

Bruker SMART CCD diffractometer	4861 reflections with $I > 2\sigma(I)$
$\omega$ rotation with narrow frames	$R_{int} = 0.040$
Absorption correction: none	$\theta_{max} = 28.41^\circ$
18 440 measured reflections	$h = -29 \rightarrow 22$
7060 independent reflections	$k = -10 \rightarrow 9$
	$l = -17 \rightarrow 23$
	Intensity decay: none

**Refinement**

Refinement on $F^2$	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.049$	$\Delta\rho_{max} = 0.317 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.115$	$\Delta\rho_{min} = -0.360 \text{ e } \text{\AA}^{-3}$
$S = 1.033$	Extinction correction: <i>SHELXTL</i>
7060 reflections	Extinction coefficient: 0.0028 (3)
392 parameters	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
H atoms: see below	
$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 1.0126P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

**Table 6. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (6)**

B1—O1	1.469 (3)	B1—O3	1.487 (3)
B1—O4	1.476 (3)	B1—O2	1.501 (3)
O1—B1—O4	113.05 (17)	O1—B1—O2	104.72 (17)
O1—B1—O3	113.08 (17)	O4—B1—O2	112.07 (17)
O4—B1—O3	104.85 (17)	O3—B1—O2	109.19 (16)

**Table 7. Hydrogen bonding geometry ( $\text{\AA}$ ,  $^\circ$ ) for structures (1)–(5)**

Compound	D—H...A	D—H	H...A	D...A	D—H...A
(1)	N—H1...O4	0.94 (3)	1.90 (3)	2.764 (3)	153 (3)
(2)	N—H1...O1	0.98 (3)	1.83 (3)	2.755 (2)	157 (2)
(3)	N—H1...O2	0.98 (2)	1.80 (2)	2.772 (2)	175 (2)
(4)	N1—H1...O4	0.92 (2)	2.01 (2)	2.854 (2)	151 (2)
(5)	N1—H1...O1	0.87 (3)	1.98 (3)	2.805 (2)	157 (3)

Each data collection nominally covered a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different  $\varphi$  angle for the crystal and each exposure covered  $0.3^\circ$  in  $\omega$ . H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds), and with  $U_{iso}$  constrained to be 1.2 (1.5 for methyl groups) times  $U_{eq}$  of the carrier atom; positional parameters for N—H and P—H H atoms were refined freely. For the non-centrosymmetric structure of (1), the combination of X-ray wavelength and elements present does not permit a determination of the absolute structure from anomalous dispersion effects.

For all compounds, data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART* for (3), local programs for all other compounds. For all compounds, data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1497). Services for accessing these data are described at the back of the journal.

**References**

- Clegg, W., Elsegood, M. R. J., Lawlor, F. J., Norman, N. C., Pickett, N. L., Robins, E. G., Scott, A. J., Nguyen, P., Taylor, N. J. & Marder, T. B. (1998). *Inorg. Chem.* **37**, 5289–5293.
- Dai, C., Johnson, S. M., Lawlor, F. J., Lightfoot, P., Marder, T. B., Norman, N. C., Orpen, A. G., Pickett, N. L., Quayle, M. J. & Rice, C. R. (1998). *Polyhedron*. In the press.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Goddard, R., Niemeyer, C. M. & Reetz, M. T. (1993). *Acta Cryst.* **C49**, 402–404.
- Graf, E., Hosseini, M. W., De Cian, A. & Fischer, J. (1996). *Bull. Soc. Chim. Fr.* **133**, 743–748.
- Graf, E., Hosseini, M. W., Ruppert, R., De Cian, A. & Fischer, J. (1995). *J. Chem. Soc. Chem. Commun.* pp. 1505–1506.
- Graf, E., Hosseini, M. W., Ruppert, R., Kyritsakas, N., De Cian, A., Fischer, J., Estournes, C. & Raulelle, F. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1115–1117.
- Griffith, W. P., White, A. J. P. & Williams, D. J. (1996). *Polyhedron*, **15**, 2835–2839.
- He, X.-M. & Hartwig, J. F. (1996). *J. Am. Chem. Soc.* **118**, 1696–1702.
- Mohr, S., Heller, G., Timper, U. & Woller, K.-H. (1990). *Z. Naturforsch. Teil B*, **45**, 308–322.
- Nguyen, P., Dai, C., Taylor, N. J., Power, W. P., Marder, T. B., Pickett, N. L. & Norman, N. C. (1995). *Inorg. Chem.* **34**, 4290–4291.
- Sheldrick, G. M. (1994). *SHELXTL. Structure Determination Programs*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995). *SMART and SAINT. Area-Detector Control and Integration Software*. Siemens Analytical X-ray Systems Inc., Madison, Wisconsin, USA.
- Westcott, S. A., Blom, H. P., Marder, T. B., Baker, R. T. & Calabrese, J. C. (1993). *Inorg. Chem.* **32**, 2175–2182.
- Westcott, S. A., Taylor, N. J., Marder, T. B., Baker, R. T., Jones, N. J. & Calabrese, J. C. (1991). *J. Chem. Soc. Chem. Commun.* pp. 304–305.