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#### Key indicators

Single-crystal X-ray study  
T = 100 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$   
R factor = 0.045  
wR factor = 0.110  
Data-to-parameter ratio = 16.1

For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

## 4-Methylpyridinium bis(pyrocatecholato- $\kappa^2\text{O},\text{O}'$ )-borate catechol solvate

Unlike the previously reported salts of the 4-methylpyridinium cation and the bis(pyrocatecholato)borate anion [Clegg *et al.* (1998). *Acta Cryst.* **C54**, 1875–1880], the title compound,  $\text{C}_6\text{H}_8\text{N}^+ \cdot \text{C}_{12}\text{H}_8\text{BO}_4^- \cdot \text{C}_6\text{H}_6\text{O}_2$ , is a solvate containing a molecule of catechol. The crystal packing is influenced by  $\text{N}-\text{H} \cdots \text{O}$  and  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bonds.

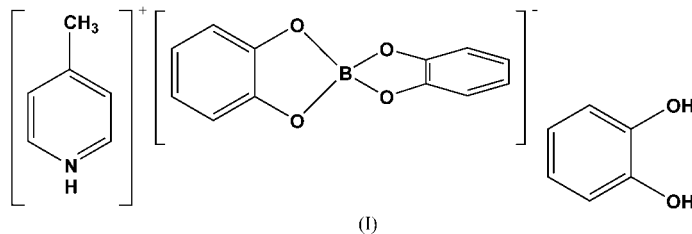
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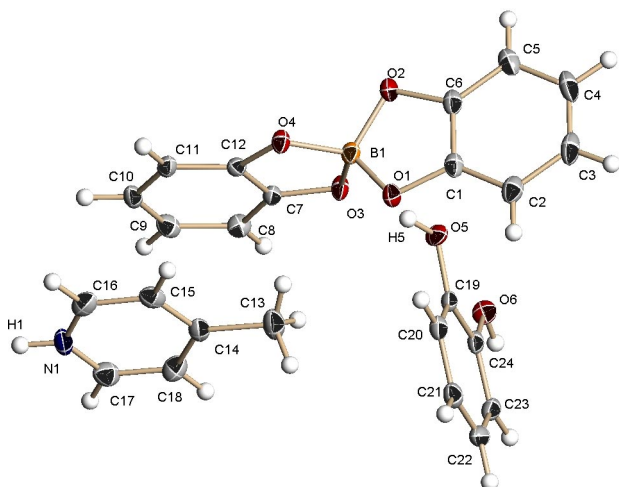
Online 12 June 2004

### Comment

In addition to the ammonium cations  $[\text{NH}_4]^+$  (Goddard *et al.*, 1993) and  $[\text{NH}_2\text{Me}_2]^+$  (Clegg, Elsegood *et al.*, 1998), the bis(pyrocatecholato)borate anion  $[\text{B}(1,2-\text{O}_2\text{C}_6\text{H}_4)_2]^-$  has been found to crystallize with a number of pyridinium cations. These include  $[2-\text{MeC}_5\text{H}_4\text{NH}]^+$  and two polymorphs containing  $[4-\text{MeC}_5\text{H}_4\text{NH}]^+$  (Clegg, Scott *et al.*, 1998).  $[\text{NHEt}_3]^+$  (Mohr *et al.*, 1990) and the unsubstituted pyridinium cation  $[\text{C}_5\text{H}_5\text{NH}]^+$  (Griffin *et al.*, 1996) also form salts with  $[\text{B}(1,2-\text{O}_2\text{C}_6\text{H}_4)_2]^-$ , although in these cases a molecule of catechol is incorporated into the structure. The structures of  $[1,10\text{-phenH}][\text{B}(1,2-\text{O}_2\text{C}_6\text{H}_4)_2]$  (phen = phenanthroline), and its dichloromethane solvate (Clegg, Scott *et al.*, 1998) have also been determined as has the structure of the phosphonium salt  $[\text{PHMe}_3][\text{B}(1,2-\text{O}_2\text{C}_6\text{H}_4)_2]$  (Clegg, Scott *et al.*, 1998) and a range of salts containing cationic rhodium or iridium phosphine complexes (Clegg *et al.*, 1999). In this paper, we report the structure of a  $[4-\text{MeC}_5\text{H}_4\text{NH}]^+$  salt of  $[(\text{C}_6\text{H}_4\text{O}_2)_2\text{B}]^-$  that, unlike the crystal structures previously reported for salts of  $[4-\text{MeC}_5\text{H}_4\text{NH}]^+$  and  $[(\text{C}_6\text{H}_4\text{O}_2)_2\text{B}]^-$  (Clegg, Scott *et al.*, 1998), but in common with the pyridinium and triethylammonium salts, includes a molecule of catechol in the structure.



The molecular structure of (I) is shown in Fig. 1. The crystal structure contains hydrogen bonds between the catechol molecules and the catecholate ligands of the  $[\text{B}(1,2-\text{O}_2\text{C}_6\text{H}_4)_2]^-$  anions. The 4-methylpyridinium cations also form hydrogen bonds to the catechol molecules, producing a ribbon structure (see Fig. 2). These ribbons crosslink through hydrogen bonds between the catecholate ligands and pyridinium cations to form a one-dimensional hydrogen-bonded polymer (see Fig. 3).



**Figure 1**

The molecular structure of (I), showing displacement ellipsoids drawn at the 50% probability level. The solvent catechol molecule has been transformed by the symmetry operation  $(x, y, z - 1)$ .

## Experimental

$B_2(\text{cat})_3$  (0.1 g, 0.029 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (4 ml) in a small Schlenk tube to which 4-picoline (0.04 g, 0.058 mmol) was added and the mixture stirred for 1 h at room temperature. After this time, hexane (4 ml) was added as an overlay and solvent diffusion over a period of days at 243 K afforded colourless crystals of  $[4\text{-MeC}_5\text{H}_4\text{NH}][\text{B}(1,2\text{-O}_2\text{C}_6\text{H}_4)_2]$ .  $\text{C}_{18}\text{H}_{16}\text{BNO}_4$  requires: N 4.35, C 67.30, H 5.00%; found: N 4.40, C 67.65, H 5.75%.  $^{11}\text{B}$   $\{^1\text{H}\}$  NMR:  $\delta$  13.2 (s). Although the microanalytical data are consistent with the formula  $[4\text{-MeC}_5\text{H}_4\text{NH}][\text{B}(1,2\text{-O}_2\text{C}_6\text{H}_4)_2]$ , confirmed by X-ray crystallography, one (colourless) crystal examined was found to have the composition  $[4\text{-MeC}_5\text{H}_4\text{NH}][\text{B}(1,2\text{-O}_2\text{C}_6\text{H}_4)_2] \cdot 1,2\text{-(HO)}_2\text{C}_6\text{H}_4$ . There are no obvious morphology differences between the two phases.

### Crystal data

$\text{C}_6\text{H}_8\text{N}^+ \cdot \text{C}_{12}\text{H}_8\text{BO}_4^- \cdot \text{C}_6\text{H}_6\text{O}_2$   
 $M_r = 431.24$   
 Monoclinic,  $P2_1/n$   
 $a = 10.0007$  (14) Å  
 $b = 12.9573$  (17) Å  
 $c = 16.396$  (3) Å  
 $\beta = 96.872$  (11)°  
 $V = 2109.3$  (6) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.355$  Mg m<sup>-3</sup>

$D_m = 1.340$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 4189 reflections  
 $\theta = 2.5\text{--}25.8^\circ$   
 $\mu = 0.10$  mm<sup>-1</sup>  
 $T = 100$  (3) K  
 Block, colourless  
 $0.05 \times 0.05 \times 0.05$  mm

### Data collection

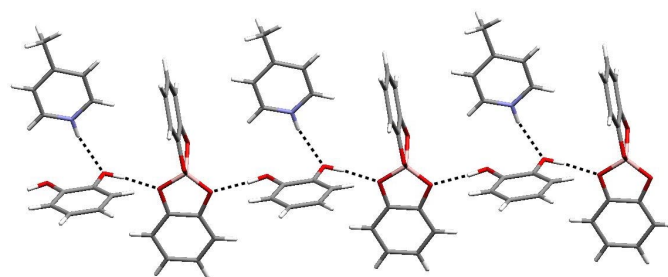
Bruker SMART APEX CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)  
 $T_{\min} = 0.929$ ,  $T_{\max} = 0.990$   
 23718 measured reflections

4828 independent reflections  
 3973 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.037$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -12 \rightarrow 12$   
 $k = -16 \rightarrow 16$   
 $l = -21 \rightarrow 21$

### Refinement

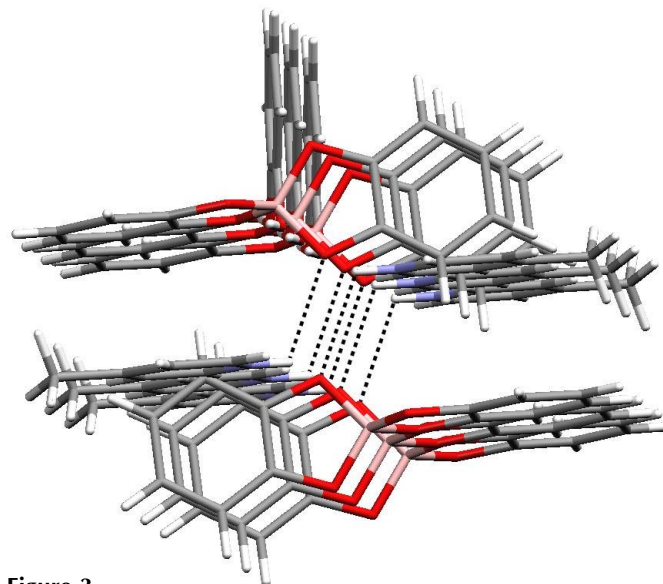
Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.110$   
 $S = 1.03$   
 4828 reflections  
 299 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 0.7965P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.29$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.25$  e Å<sup>-3</sup>



**Figure 2**

Stick representation (colour code: C grey, H white, O red, B pink, N blue) of the hydrogen-bonded (dashed lines) ribbon polymers formed in (I).



**Figure 3**

Cross-linking hydrogen bonds (dashed lines) between ribbons in (I). The colour code is as in Fig. 2.

**Table 1**

Selected geometric parameters (Å, °).

C1—O1	1.3662 (17)	B1—O1	1.4746 (19)
C6—O2	1.3681 (17)	B1—O4	1.4820 (19)
C7—O3	1.3659 (17)	C19—O5	1.3731 (17)
C12—O4	1.3756 (16)	C24—O6	1.3664 (18)
B1—O2	1.4742 (19)		
O2—B1—O1	105.58 (11)	O4—B1—O3	103.32 (11)
O2—B1—O4	112.77 (12)	C1—O1—B1	105.89 (11)
O1—B1—O4	113.49 (12)	C6—O2—B1	105.98 (11)
O2—B1—O3	111.09 (12)	C7—O3—B1	108.12 (11)
O1—B1—O3	110.74 (12)	C12—O4—B1	108.15 (11)

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
N1—H1 $\cdots$ O2	0.872 (15)	2.425 (18)	2.8864 (17)	113.6 (14)
N1—H1 $\cdots$ O5 <sup>i</sup>	0.872 (15)	2.096 (17)	2.8621 (18)	146.3 (16)
N1—H1 $\cdots$ O6 <sup>i</sup>	0.872 (15)	2.587 (17)	3.1073 (18)	119.2 (14)
O5—H5 $\cdots$ O3 <sup>ii</sup>	0.864 (15)	1.788 (16)	2.6469 (15)	172.5 (17)
O6—H6 $\cdots$ O4 <sup>iii</sup>	0.871 (15)	1.793 (16)	2.6600 (15)	173.5 (18)

Symmetry codes: (i)  $x, y, z - 1$ ; (ii)  $2 - x, 1 - y, 1 - z$ ; (iii)  $1 - x, 1 - y, 1 - z$ .

The NH H atom of the pyridinium cation and all hydroxy H atoms were located in difference maps. Distance restraints of 0.88 (3) and 0.84 (3) Å were applied to the N—H and O—H bond lengths, respectively. Methyl H atoms were located using a rotating group refinement, with C—H bond lengths constrained to 0.96 Å. All other H atoms were positioned in ideal geometries and refined by riding on their carrier atom. All H atoms were assigned displacement parameters equal to 1.5 times (methyl and hydroxyl H atoms) or 1.2 times (all other H atoms)  $U_{eq}$  of their parent atom.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE* and *SHELXTL* (Bruker, 2002); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

## References

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