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Tris[(1-methylimidazol-2-yl)methyl]-amine–boric acid (1/1)

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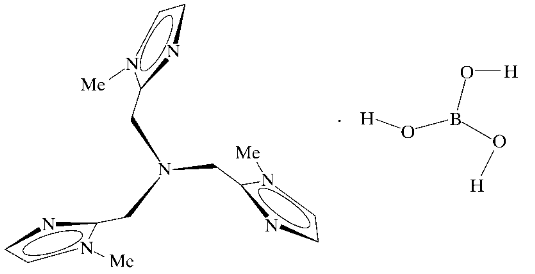
Cocrystallization of a polyimidazole compound with boric acid results in the formation of the title compound, $C_{15}H_{21}N_7{\cdot}B(OH)_3$, which has an extensive hydrogen-bonding network. The O$\cdots$N(im) separations (im is imidazole) range from 2.6991 (15) to 2.7914 (14) Å, with O—H$\cdots$N angles ranging from 170.6 (18) to 175 (2)°. In addition, symmetry-related boric acid molecules form intermolecular hydrogen bonds, with an O$\cdots$O distance of 2.7582 (14) Å, and symmetry-related imidazole groups form π–π stacks, with a centroid-to-centroid separation of 3.533 Å.

Comment

The donor–acceptor properties of $B(OH)_3$ are well known (Farmer, 1982; Coddington & Taylor, 1989). In neutral aqueous solutions, $B(OH)_3$ generally behaves as a Lewis acid (Farmer, 1982), forming $B(OH)_4^-$ anions rather than the conjugate base, $BO(OH)_2^-$, which has been observed in the solid state in $[Cu_2\{BO(OH)_2\}(OH)_3]$ (Behm & Baerlocher, 1985) and $(Et_4N)_2[BO(OH)_2]_2B(OH)_3{\cdot}5H_2O$ (Freyhardt & Wiebcke, 1994). Boric acid is also known to cocrystallize with urea, forming supramolecular structures containing complex intermolecular hydrogen-bonding networks (Li *et al.*, 1999). These compounds and their derivatives are of interest as host lattices for the inclusion (Li & Mak, 1997*a*) of small molecules and ions (Li & Mak, 1997*b*). With this in mind, the present study explores the potential use of boric acid in the crystallization of heterocyclic polyamine compounds, such as the polyimidazole ligand tris[(1-methylimidazol-2-yl)methyl]-amine (tmima). As with many polyimidazole compounds (Chen *et al.*, 1994), tmima is hygroscopic and does not crystallize readily using conventional crystallization methods. We describe here a general method for crystallizing *N*-alkylated imidazole compounds in the presence of boric acid, and the X-ray crystal structure of the resulting tmima–boric acid complex, the title compound, (I).

Compound (I) crystallizes with one tmima and boric acid molecule per asymmetric unit; the structures of the independent tmima and boric acid molecules are shown in Fig. 1. The tmima molecule has approximate threefold symmetry, with the imidazole pendants oriented in a paddle-wheel arrangement around the amine atom N1. The imidazole C—C and C—N distances and C—C—N and C—N—C angles are normal and consistent with other imidazole compounds (Richardson *et al.*, 1988). The boric acid molecule is planar and has local C_{3h} symmetry. The B—O distances and O—B—O angles are consistent with the values reported for other boric acid structures (Andrews *et al.*, 1983), and all three $B(OH)_3$ H atoms are involved in hydrogen bonding.



(I)

The packing arrangement in (I) (Fig. 2) shows the presence of an extended intermolecular hydrogen-bonding network between the tmima and boric acid molecules in the *ac* plane and projected along the crystallographic *b* axis. These layers are slightly less than one unit cell deep along the *a* axis, and are separated by hydrophobic boundaries composed of imidazole N—CH_3 and ring H atoms (a figure showing the packing in the *ac* plane is available in the supplementary material).

The two types of hydrogen-bonding interactions are illustrated in Fig. 2. The first involves bonds between boric acid molecules and different imidazole pendants of neighboring tmima molecules. The $O1^i\cdots N6^i$ [2.7914 (14) Å] and $O3^i\cdots N2$ [2.6991 (15) Å] separations, as well as the $O1^i—H1O^i\cdots N6^i$ [170.6 (18)°] and $O3^i—H3O^i\cdots N2$ [175 (2)°] angles, indicate strong hydrogen bonding between different tmima pendants

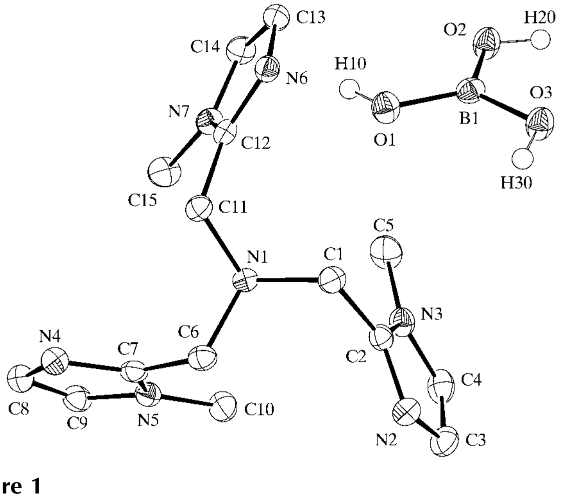


Figure 1
A view of the two molecular components of (I), shown with 50% probability displacement ellipsoids. Methyl and methylene H atoms have been omitted for clarity.

and boric acid molecules (see Table 1). A second type of hydrogen bonding occurs between symmetry-related $B(OH)_3$ molecules. The resulting eight-membered ring formed *via* two O···H bonds is planar, and the $O2^{iii}\cdots O3^{i}$ [2.7582 (14) Å] separation and $O2^{iii}-H2O^{iii}\cdots O3^{i}$ [173 (2)°] angle indicate strong hydrogen bonding between $B(OH)_3$ molecules (Fig. 2 and Table 1).

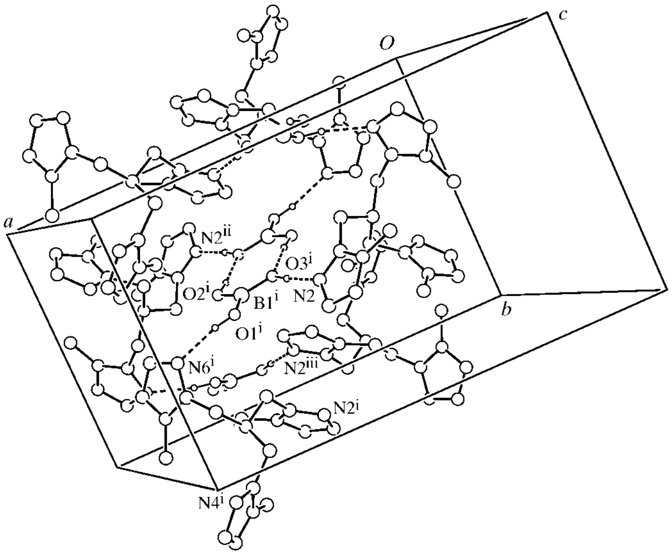


Figure 2
A packing diagram for (I), displaying the hydrogen-bonding interactions between imidazole rings and boric acid molecules, and the π–π-stacking interactions between imidazole rings containing atom N2. The symmetry codes are as in Table 1, plus (iii) $x, \frac{1}{2} - y, z - \frac{1}{2}$.

Fig. 2 also shows the intermolecular π–π-stacking interactions between tmima molecules. Imidazole rings containing atom N2 form π–π stacks around inversion centers. The separation between imidazole ring centroids is 3.533 Å, indicative of strong π–π interactions between the imidazole rings. Curiously, the third imidazole pendant, containing atom N4, is involved in neither hydrogen bonding nor π–π stacking, but rather is oriented towards the methyl groups of neighboring tmima molecules, which are part of the hydrophobic boundary between hydrogen-bonding layers. The closest H···H contact between layers is 2.56 Å.

In conclusion, we have established the effectiveness of boric acid for inducing crystallization of the polyimidazole compound tmima. The crystal structure shows an interesting hydrogen-bonding network between imidazole and boric acid molecules along the crystallographic *b* axis, as well as π–π-stacking interactions between imidazole groups.

Experimental

Tris[(1-methylimidazol-2-yl)methyl]amine (tmima) was prepared according to the procedure of Oberhausen *et al.* (1990). Crystallization of tmima was induced by addition of boric acid (0.052 g, 0.84 mmol) dissolved in ethyl acetate (1 ml) containing H_2O (5%) and tmima (0.25 g, 0.84 mmol). The resulting solution was carefully layered with diethyl ether and large colorless single crystals of (I) formed after 12 h at 298 K.

Crystal data

$C_{15}H_{21}N_7\cdot H_3BO_3$
$M_r = 361.22$
Monoclinic, $P2_1/c$
$a = 16.2812$ (17) Å
$b = 10.001$ (1) Å
$c = 12.2564$ (13) Å
$\beta = 110.72$ (2)°
$V = 1866.6$ (3) Å^3
$Z = 4$
$D_x = 1.285$ Mg m^{-3}
$D_m = 1.28$ Mg m^{-3}
D_m measured by pycnometry
Mo $K\alpha$ radiation
Cell parameters from 6545 reflections
$\theta = 2.4$–28.1°
$\mu = 0.09$ mm^{-1}
$T = 100$ (2) K
Plate, colorless
0.24 × 0.21 × 0.08 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{\min} = 0.90$, $T_{\max} = 0.99$
16 065 measured reflections
4361 independent reflections
3542 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$
$\theta_{\max} = 28.3°$
$h = -21 \rightarrow 20$
$k = -13 \rightarrow 13$
$l = -15 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.110$
$S = 1.03$
4361 reflections
250 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0440P)^2 + 0.7596P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.028$
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1-H1O\cdots N6$	0.88 (2)	1.92 (2)	2.7914 (14)	170.6 (18)
$O3-H3O\cdots N2^{i}$	0.90 (2)	1.81 (2)	2.6991 (15)	175 (2)
$O2-H2O\cdots O3^{ii}$	0.87 (2)	1.90 (2)	2.7582 (14)	173 (2)

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $1 - x, -y, 1 - z$.

The imidazole and methylene H atoms were calculated and included as fixed contributions, with $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$. The methyl groups were calculated and allowed to ride (the torsion angle which defines the orientation was allowed to refine) on the attached C atom, and these atoms were assigned $U_{\rm iso}(H) = 1.5U_{\rm eq}(C)$. Fixed C—H distances were in the range 0.95–0.99 Å. The H atoms of the boric acid molecule were located in difference Fourier maps and refined isotropically.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1390). An additional figure is also available. Services for accessing these data are described at the back of the journal.

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