

Dipotassium maleate with boric acid

Mustafa Tombul,^{a*} Kutalmis Guven,^b Orhan Büyükgüngör,^c Huseyin Aktas^b and Tahsin Nuri Durlu^d

^aDepartment of Chemistry, Faculty of Arts and Sciences, University of Kirikkale, Yahsihan Kirikkale Campus, 71450 Kirikkale, Turkey, ^bDepartment of Physics, Faculty of Arts and Sciences, University of Kirikkale, Yahsihan Kirikkale Campus, 71450 Kirikkale, Turkey, ^cDepartment of Physics, Ondokuz Mayıs University, TR-55139 Samsun, Turkey, and ^dDepartment of Physics, Faculty of Science, University of Ankara, Beşevler, 06100 Ankara, Turkey
Correspondence e-mail: mustafatombul38@gmail.com

Received 8 June 2007

Accepted 24 July 2007

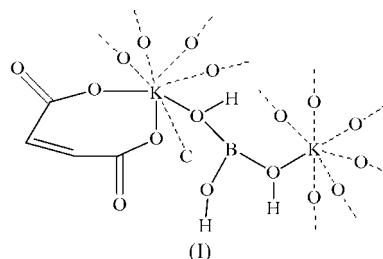
Online 24 August 2007

In the title compound, poly[$(\mu_3$ -boric acid)- μ_4 -maleato-dipotassium], $[\text{K}_2(\text{C}_4\text{H}_2\text{O}_4)\{\text{B}(\text{OH})_3\}]_n$, there are two independent K^+ cations, one bonded to seven O atoms (three from boric acid and four from maleate), and the other eight-coordinate *via* three boric acid and four maleate O atoms and a weak η^1 -type coordination to the $\text{C}=\text{C}$ bond of the maleate central C atoms. Hydrogen bonding links the boric acid ligands and maleate dianions, completing the packing structure.

Comment

It has been well established that orthoboric acid, $\text{B}(\text{OH})_3$, is the archetype and primary source of oxo-boron compounds (Freyhard & Wiebcke, 1994; Li *et al.*, 1999). In most cases, it does not behave as a Brønsted acid with the formation of the conjugate-base anion $[\text{BO}(\text{OH})_2]^-$, but rather as a Lewis acid with the formation of the tetrahedral anion $[\text{B}(\text{OH})_4]^-$ (Farmer, 1982; Coddington & Taylor, 1989). In dilute aqueous solution, this monobasic acid exists almost solely as an equilibrium mixture of undissociated molecular $\text{B}(\text{OH})_3$ and the tetrahydroxyborate anion $\text{B}(\text{OH})_4^-$. At higher concentrations, secondary equilibria involving condensation reactions of the two dominant monomeric species take place, giving oligomers such as the triborate monoanion $[\text{B}_3\text{O}_3(\text{OH})_4]^-$, the triborate dianion $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$, the tetraborate $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ and the pentaborate $[\text{B}_5\text{O}_6(\text{OH})_4]^-$. Hence, several interesting supramolecular hydrogen-bonded architectures involving tetrahydroxypentaborate and boric acid incorporating a tertiary or quarternary ammonium ion have been isolated and characterized in recent years (Turdybecov *et al.*, 1992; Loboda *et al.*, 1994; Freyhard *et al.*, 1994; Li & Mak, 1997). However, hydrogen-bonded structures containing only monomeric borate species are rare. In $(\text{CH}_3)_4\text{N}^+\cdot\text{BO}(\text{OH})_2^- \cdot 2(\text{NH}_2)_2\text{CO}\cdot\text{H}_2\text{O}$ and $(\text{Et}_4\text{N})_2[\text{BO}(\text{OH})_2]\cdot\text{B}(\text{OH})_3\cdot 5\text{H}_2\text{O}$, the $\text{BO}(\text{OH})_2^-$ unit is present in the host lattice (Li *et al.*, 1999;

Freyhard *et al.*, 1994). The three structures $[(\text{C}_2\text{H}_5)_4\text{N}^+]_2\cdot\text{CO}_3^{2-}\cdot(\text{NH}_2)_2\text{CO}\cdot 2\text{B}(\text{OH})_3\cdot\text{H}_2\text{O}$, $[(\text{PPh}_3)_2\text{N}^+\cdot\text{Cl}^-]\cdot\text{B}(\text{OH})_3$ and the 1:2 adduct of melamine with boric acid (Li *et al.*, 1999; Andrews *et al.*, 1983; Roy *et al.*, 2002) would appear to be the only structures known to date containing the undissociated $\text{B}(\text{OH})_3$ unit. We report here the synthesis and crystal structure of the title compound, (I), a crystalline solid in which, remarkably, both the $\text{B}(\text{OH})_3$ molecule and the dipotassium maleate salt co-exist in an unusual coordination mode.



The basic fragment of (I), with the asymmetric unit formula $[\text{K}_2(\text{C}_4\text{H}_2\text{O}_4)\cdot\text{B}(\text{OH})_3]$, is illustrated in Fig. 1, and geometric parameters are given in Table 1. The structure may be conveniently described as two crystallographically independent K atoms located between the two types of ligands, *viz.* boric acid molecules and maleate anions, which form bonds to the K atoms *via* their O atoms. There are weak hydrogen bonds linking the boric acid and maleate dianions; each $\text{B}(\text{OH})_3$ unit interacts with three maleate ligands through $\text{O}\cdots\text{H}\cdots\text{O}$ bonds. All hydrogen bonds linking adjacent boric acid and maleate dianions are donated exclusively by $\text{B}(\text{OH})_3$ molecules [$\text{O}\cdots\text{O} = 2.618(1)\text{--}2.689(3)\text{ \AA}$ and $\text{O}\cdots\text{H}\cdots\text{O} = 163.4(1)\text{--}165.9(1)^\circ$] (Table 2). The K atoms reside between the layers, linked by bonds to the O atoms of the layers. This connectivity of hydrogen bonds and $\text{K}\text{--}\text{O}$ bonds give rise to the three-dimensional structure (Fig. 2).

Three O atoms (O1, O2 and O3) are bonded to the B atom to form a BO_3 triangle. The average value of the three $\text{O}\text{--}\text{B}\text{--}\text{O}$ angles around boron is $119.99(19)^\circ$, which compares with the usual average trigonal value of 120.0° . The mean $\text{B}\text{--}\text{O}$ distance of $1.363(3)\text{ \AA}$ is in good agreement with the reported trigonal $\text{B}\text{--}\text{O}$ distances in $[(\text{C}_2\text{H}_5)_4\text{N}^+]_2\cdot\text{CO}_3^{2-}\cdot(\text{NH}_2)_2\text{CO}\cdot 2\text{B}(\text{OH})_3\cdot\text{H}_2\text{O}$ (1.362 \AA), $[(\text{PPh}_3)_2\text{N}^+\cdot\text{Cl}^-]\cdot\text{B}(\text{OH})_3$ (1.36 \AA)

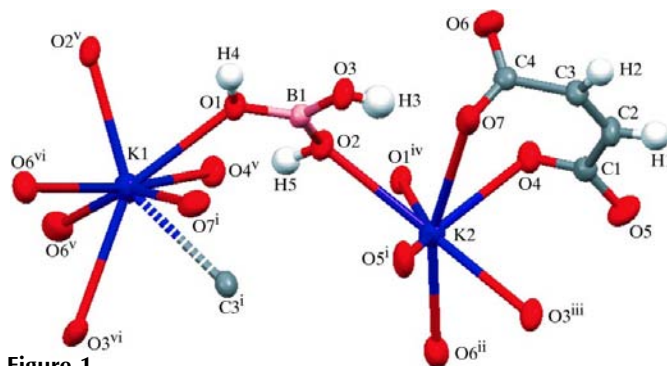


Figure 1
The coordination environment of the K atoms in (I). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + \frac{3}{2}, -y + 1, z + \frac{1}{2}$; (iii) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (iv) $-x + 2, y + \frac{1}{2}, -z + \frac{3}{2}$; (v) $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$; (vi) $-x + \frac{3}{2}, y, z + \frac{1}{2}$.]

and the 1:2 adduct of melamine with boric acid (1.362 Å) (Li *et al.*, 1999; Andrews *et al.*, 1983; Roy *et al.*, 2002).

The potassium centres in (I) display very different coordination geometries. Most of the K—O distances are slightly longer than the sum of the covalent radii (2.69 Å; Allen *et al.*, 1987) but may be considered weak ionic bonds owing to their directionality; other K—O distances are considerably longer (Table 1). Atom K2 is seven-coordinate; the coordination polyhedron is a distorted monocapped trigonal prism with O5^{vii} as the capping atom (Fig. 1; symmetry code as in Fig. 1). The K2—O coordination distances are between 2.695 (2) and 2.962 (2) Å (mean 2.84 Å), in agreement with the average K—O distance for KO₇ moieties [Cambridge Structural Database, Version 5.25; 2.80 (11) Å for 446 observations; Allen, 2002]. Atom K1 is eight-coordinate, through atoms O1, O2^v and O3^{vi} from three different boric acid molecules, O4^v, O6^v, O6^{vi} and O7ⁱ from four different maleate ligands, and an η¹-type coordination to C3 of the C=C bond (Fig. 1; symmetry codes as in Fig. 1). The K1—O coordination distances range from 2.754 (2) to 3.206 (2) Å (mean 2.95 Å). Organometallic complexes of potassium metal or K⁺ that exhibit both η¹- and η²-coordination are well known (Kuhl *et al.*, 1999; Chitsaz & Neumuller, 2001; Ganesan *et al.*, 2002); the K—C distances are typically in the range 2.9–3.5 Å. Although potassium readily forms organometallic complexes with coordination numbers as high as η⁸ to a single ligand in the case of bicyclic aromatic species (Cloke *et al.*, 2000) or the cyclooctatetraenyl anion (Xia *et al.*, 1991), there are only two reported structures in the literature containing K⁺—C=C η¹-type compounds (McPherson *et al.*, 1978; Noordik *et al.*, 1974). The closest distance between K atoms is K1^v···K2 of 3.877 (8) Å (symmetry code as in Fig. 1).

The title compound has a unique structure, with no directly comparable compounds containing K atoms coordinated by

both dicarboxylic acid and boric acid moieties. Previously reported related examples are found in the structures of potassium dimalatoborate monohydrate (Zviedre & Kolesnikova, 1983), potassium dicitratoborate dihydrate (Zviedre *et al.*, 1984), potassium bis(salicylato)borate salicylic acid (Zviedre *et al.*, 1992) and poly[[μ₆-bis(oxalato)borate]-potassium] (Zavalij *et al.*, 2003). In these examples, however, the dicarboxylate moieties are bonded directly to tetrahedrally coordinated B atoms. The successful synthesis of the title compound under atmospheric pressure may help in the search for new ways of synthesizing borate crystals with interesting structural features.

Experimental

The title compound was prepared by dissolving KOH (0.05 mol, 2.8 g) and B(OH)₃ (1 mol, 0.62 g) in H₂O (20 ml). To this solution, a solution of maleic acid (0.02 mol, 2.32 g) in H₂O (20 ml) was added dropwise at room temperature, producing a colourless solution. The reaction mixture was stirred at 323 K for 9 h, yielding a white solid. Single crystals of (I) suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated aqueous solution at 298 K (yield 2.1 g, 83% based on boric acid). ¹H NMR (D₂O, 298 K, TMS): δ 6.02 (2H, s, HC=CH); ¹³C NMR (D₂O, 298 K, TMS): δ 130.80 (COOH), 175.51 (HC=CH). IR spectra were recorded from a KBr disc, using a Jasco 680 Plus FT-IR spectrometer. IR (cm⁻¹): ν(*br*, O—H) 3366, ν(*w*, C=C) 1633, ν(*s*, C=O_{asym}) 1561, ν(*s*, C=O_{sym}) 1399–1306.

Crystal data

[K ₂ (C ₄ H ₂ O ₄)(H ₃ BO ₃)]	<i>V</i> = 892.14 (14) Å ³
<i>M_r</i> = 254.09	<i>Z</i> = 4
Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁	Mo <i>K</i> α radiation
<i>a</i> = 6.4968 (5) Å	μ = 1.07 mm ⁻¹
<i>b</i> = 10.2591 (11) Å	<i>T</i> = 296 (2) K
<i>c</i> = 13.3852 (10) Å	0.53 × 0.52 × 0.40 mm

Data collection

Stoe IPDSII diffractometer	5260 measured reflections
Absorption correction: integration	1748 independent reflections
(<i>X-RED32</i> ; Stoe & Cie, 2002)	1717 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T</i> _{min} = 0.520, <i>T</i> _{max} = 0.652	<i>R</i> _{int} = 0.065

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.027	Δρ _{max} = 0.25 e Å ⁻³
<i>wR</i> (<i>F</i> ²) = 0.071	Δρ _{min} = -0.36 e Å ⁻³
<i>S</i> = 1.05	Absolute structure: Flack (1983),
1748 reflections	with 711 Friedel pairs
148 parameters	Flack parameter: 0.01 (4)
H atoms treated by a mixture of independent and constrained refinement	

The maleate H atoms were constrained to an ideal geometry, with C—H distances of 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C). Atoms H4 and H5 of the boric acid were also constrained to an ideal geometry, with O—H distances of 0.98 Å and with *U*_{iso}(H) = 1.5*U*_{eq}(C). Atom H3 was located in a difference Fourier synthesis and refined isotropically.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Mercury* (Version 1.4.1; Macrae *et al.*, 2006); software used to prepare material for publication: *enCIFer* (Version 1.2; Allen *et al.*, 2004).

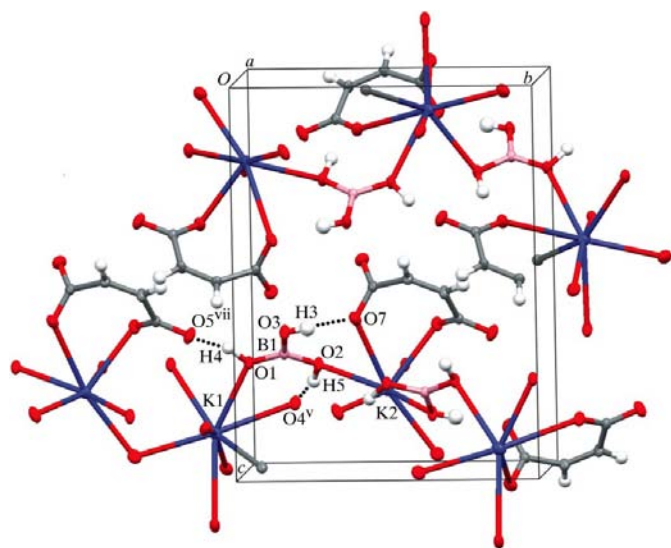


Figure 2

A packing diagram for complex (I). Dashed lines represent hydrogen bonds. One set of labels for atoms involved in the hydrogen bonds are shown (see Table 2 for details and symmetry codes).

Table 1

Selected geometric parameters (Å, °).

K2—O5 ⁱ	2.6952 (19)	C1—C2	1.485 (3)
K2—O4	2.7778 (18)	C3—C2	1.321 (3)
K2—O6 ⁱⁱ	2.8380 (19)	C3—C4	1.492 (3)
K2—O3 ⁱⁱⁱ	2.8340 (18)	K1—O6 ^v	2.785 (2)
K2—O1 ^{iv}	2.8879 (16)	K1—O6 ^{vi}	2.880 (2)
K2—O2	2.8905 (16)	K1—O2 ^v	2.8907 (18)
K2—O7	2.962 (2)	K1—O7 ⁱ	3.004 (2)
O3—B1	1.364 (3)	K1—O3 ^{vi}	3.1462 (18)
O4—C1	1.252 (3)	K1—O4 ^v	3.2062 (19)
O6—C4	1.253 (3)	K1—C3 ⁱ	3.301 (2)
O7—C4	1.245 (3)	K1—O1	2.7547 (16)
O5—C1	1.253 (3)		
O2—B1—O1	119.54 (18)	O1—B1—O3	119.83 (19)
O2—B1—O3	120.60 (19)		

 Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + \frac{3}{2}, -y + 1, z + \frac{1}{2}$; (iii) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (iv) $-x + 2, y + \frac{1}{2}, -z + \frac{3}{2}$; (v) $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$; (vi) $-x + \frac{3}{2}, -y, z + \frac{1}{2}$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O2—H5 ⁱ ··O4 ^v	0.98 (1)	1.73 (1)	2.689 (3)	166 (1)
O3—H3 ⁱ ··O7	0.79 (4)	1.88 (4)	2.645 (2)	165 (4)
O1—H4 ⁱ ··O5 ^{viii}	0.98 (1)	1.66 (1)	2.618 (1)	163 (1)

 Symmetry codes: (v) $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$; (viii) $x, y - 1, z$.

The authors gratefully acknowledge Kırıkkale University for financial support of this research and the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the Stoe IPDSII diffractometer (purchased under grant F.279 of the University Research Fund).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3059). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Andrews, S. J., Robb, D. A. & Welch, A. J. (1983). *Acta Cryst.* **C39**, 880–882.
- Chitsaz, S. & Neumuller, B. (2001). *Organometallics*, **20**, 2338–2344.
- Cloke, F. G. N., Kuchta, M. C., Harker, R. M., Hitchcock, P. B. & Parry, J. S. (2000). *Organometallics*, **19**, 5795–5798.
- Coddington, J. M. & Taylor, M. J. (1989). *J. Coord. Chem.* **20**, 27–38.
- Farmer, J. B. (1982). *Adv. Inorg. Chem. Radiochem.* **25**, 187–237.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Freyhard, C. C. & Wiebcke, M. (1994). *J. Chem. Soc. Chem. Commun.* pp. 1675–1676.
- Freyhard, C. C., Wiebcke, M., Felsche, J. & Engelhardt, G. J. (1994). *J. Inclusion Phenom. Macrocycl. Chem.* **18**, 161–175.
- Ganesan, M., Berube, C. D., Gamborotta, S. & Yap, G. P. A. (2002). *Organometallics*, **21**, 1707–1713.
- Kuhl, O., Sieler, J. & Hey-Howkins, E. (1999). *Z. Kristallogr.* **214**, 496–499.
- Li, Q. & Mak, T. C. W. (1997). *Supramol. Chem.* **8**, 147–156.
- Li, Q., Xue, F. & Mak, T. C. W. (1999). *Inorg. Chem.* **38**, 4142–4145.
- Loboda, N. V., Antipin, M. Yu., Struchkov, Yu. T., Skvortsov, V. G., Petrova, O. V. & Sadetdinov, Sh. V. (1994). *Zh. Neorg. Khim.* **39**, 547–549.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- McPherson, A. M., Stucky, G. & Lehmkuhl, H. (1978). *J. Organomet. Chem.* **152**, 367–375.
- Noordik, J. H., van den Hark, T. E. M., Mooij, J. J. & Klaassen, A. A. K. (1974). *Acta Cryst.* **B30**, 833–835.
- Roy, A., Choudhury, A. & Rao, C. N. R. (2002). *J. Mol. Struct.* **613**, 61–66.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED32* (Version 1.04). Stoe & Cie, Darmstadt, Germany.
- Turdybecov, K. M., Struchkov, Yu. T., Akimov, V. M., Skvortsov, V. G., Petrova, O. V. & Sadetdinov, Sh. V. (1992). *Zh. Neorg. Khim.* **37**, 1250–1254.
- Xia, J., Jin, Z. & Chen, W. (1991). *J. Chem. Soc. Chem. Commun.* pp. 1214–1215.
- Zavalij, P. Y., Yang, S. & Whittingham, M. S. (2003). *Acta Cryst.* **B59**, 753–759.
- Zviedre, I. I., Bel'skii, V. K. & Schwartz, E. M. (1992). *Latv. Khim. Zh.* pp. 418–422.
- Zviedre, I. I., Fundamenskii, V. S., Krasnikov, V. V. & Kolesnikova, G. P. (1984). *Zh. Strukt. Khim.* **25**, 95–99.
- Zviedre, I. I. & Kolesnikova, G. P. (1983). *Izv. Akad. Nauk Latv. SSR Ser. Khim.* pp. 19–24.