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HgB_4O_7, a member of the isotypic $M^{II}B_4O_7$ family (M^{II} = Mg, Mn, Zn, Cd)

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Mercury(II) tetraborate, HgB_4O_7, belongs to the family of isotypic compounds with the formula $M^{II}B_4O_7$ (M^{II} = Mg, Mn, Zn, Cd). The structure is composed of a framework of $[B_4O_7]^{2-}$ units, with two B atoms in triangular and two B atoms in tetrahedral coordination, and an Hg^{2+} atom situated in the cavities of the framework with a [4 + 3]-coordination by O atoms.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(O–B) = 0.005 Å
R factor = 0.025
wR factor = 0.056
Data-to-parameter ratio = 13.8

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

Comment

Up to now, three phases have been synthesized in the system $HgO–B_2O_3$, *viz*. the orthoborate $Hg_3(BO_3)_2$, the tetraborate HgB_4O_7 (Chrétien & Priou, 1970), and the metaborate $Hg_4O(BO_2)_6$, which was prepared by application of high-pressure/high-temperature conditions (Chang & Margrave, 1967). For all three compounds, polycrystalline products were obtained during synthesis, but only the structure of $Hg_3(BO_3)_2$ was refined from X-ray powder data, using the Rietveld method (Laureio *et al.*, 1991). For the other two compounds powder data were published. During a systematic investigation of the preparation and crystal chemistry of various mercury oxo compounds, a method of synthesis was established for mercury(II) borates which led to the single-crystal

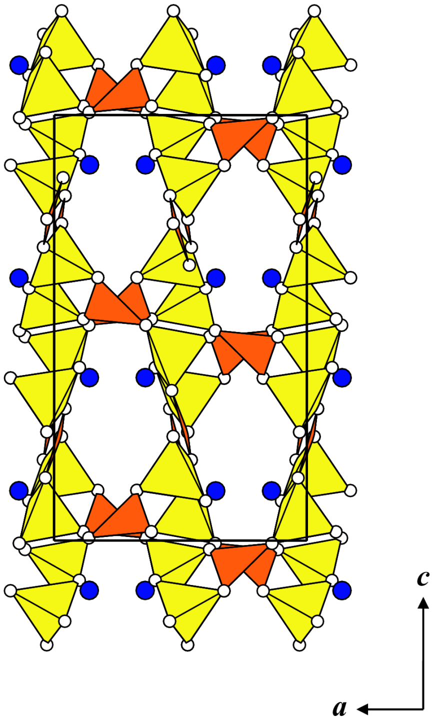

Figure 1
Projection of the structure along [010]. The Hg atoms are shown as solid blue spheres and the O atoms as white spheres. BO_4 groups (yellow) and BO_3 groups (orange) are represented as polyhedra. For clarity, Hg—O bonds have been omitted.

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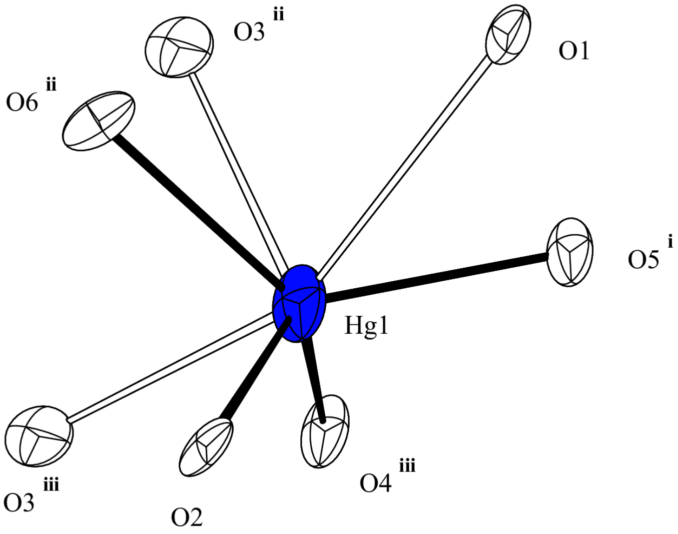

Figure 2
The [4 + 3]-coordination around the Hg atom, with displacement ellipsoids drawn at the 90% probability level. Short Hg—O bonds are given as solid lines and longer bonds as open lines.

growth of $Hg_3(BO_3)_2$ and HgB_4O_7. Owing to the higher precision of single-crystal structure analysis, the structure of $Hg_3(BO_3)_2$ was redetermined (Weil, 2003), and the structure of HgB_4O_7 is reported here for the first time.

Tetraborates of divalent metals with the general composition MB_4O_7 crystallize in different structure types depending on the ionic radii of the corresponding metals. A rough distinction between the resulting structure types can be made for metals with an ionic radius greater and smaller than 1.10 Å [ionic radii according to Shannon (1976)]. For those metals with an ionic radius > 1.10 Å, both M = Ca (Zayakina & Brovkin, 1977) and Ba (Block & Perloff, 1965) crystallize in a unique structure type, whereas phases with M = Sr (Krogh-Moe, 1964; Perloff & Block, 1966), Eu (Machida *et al.*, 1980) and Pb (Corker & Glazer, 1996) crystallize isotypically owing to the similar radii of the metals. For all metals with an ionic radius < 1.10 Å, including M = Mg (Bartl & Schuckmann, 1966), Mn (Abrahams *et al.*, 1974), Zn (Martinez-Ripoll *et al.*, 1971), Cd (Ihara & Krogh-Moe, 1966) and the title compound M = Hg, the same structure type is realised. For the sake of completeness, it should be mentioned that very recently the structure of β–ZnB_4O_7 was determined (Huppertz & Heymann, 2003); this exhibits an as yet unknown structure. This phase was prepared under extreme high-pressure/high-temperature conditions and therefore shows a different crystal chemistry compared to the other MB_4O_7 phases obtained under normal pressure.

The anionic framework structure of the title compound is composed of two crystallographically independent BO_3 triangles and two BO_4 tetrahedra, which form $[B_4O_7]^{2-}$ units by sharing common vertices. The metal atoms are situated in the cavities of this arrangement (Fig. 1).

Both BO_3 and BO_4 polyhedra show point group symmetry 1 and therefore are distorted from the ideal geometry of an equilateral triangle and a tetrahedron, respectively. The mean B—O distances are 1.371 Å for the BO_3 groups and 1.474 Å for the BO_4 groups. These values compare very well with the mean bond lengths of $\bar{d}$(B—O) = 1.370 (19) Å calculated from 75 BO_3 triangles (Zobetz, 1982) and of $\bar{d}$(B—O) = 1.476 (35) Å calculated from 242 tetrahedral BO_4 groups (Zobetz, 1990). The Hg atom is surrounded by four close O atoms [$\bar{d}(\text{Hg—O})_{\text{short}}$ = 2.233 Å] in a distorted tetrahedral arrangement. The coordination polyhedron is augmented by three remote O atoms [$\bar{d}(\text{Hg—O})_{\text{long}}$ = 2.863 Å], resulting in an overall mean Hg—O distance of 2.503 Å. Except for O2, which is the bridging atom of two BO_4 tetrahedra, all O atoms act as bridging atoms between BO_3 and BO_4 groups. The coordination numbers of the corresponding O atoms are 2 (O7), 3 (O1, O2, O4, O5 and O6) and 4 (O3). The twofold coordinate O atom is exclusively bonded to two B atoms [bridging angle B4—O7—B3 = 121.2 (4)°]. Each of the threefold coordinate O atoms is surrounded by two B and one Hg atom in a distorted trigonal environment, and the fourfold coordinate O atom shows interactions with two B and two Hg atoms, resulting in a distorted tetrahedron as the corresponding coordination polyhedron.

Experimental

Stoichiometric amounts of B_2O_3 (Merck, p. A.) and HgO (Merck, p. A.) were heated in a sealed and evacuated silica tube at 723 K for 2 d, yielding a colourless to light-yellow polycrystalline mixture and some additional droplets of elemental mercury. Application of a temperature gradient 773 → 723 K for 2 d led to the formation of colourless single crystals with a parallelepiped-like habit and an edge-length of up to 3 mm at the colder zone of the tube.

Crystal data

HgB_4O_7
M_r = 355.83
Orthorhombic, *Pbca*
a = 8.3994 (13) Å
b = 8.8066 (6) Å
c = 14.1370 (17) Å
V = 1045.7 (2) Å^3
Z = 8
D_x = 4.520 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 12.7–18.8°
μ = 29.42 mm^{-1}
T = 293 (2) K
Parallelepiped, colourless
0.27 × 0.20 × 0.11 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: numerical [the crystal shape was optimized by minimizing the R_{int} value of selected ψ-scanned reflections (*HABITUS*; Herrendorf, 1993–1997)]
$T_{\min}$ = 0.020, $T_{\max}$ = 0.177
11114 measured reflections

1516 independent reflections
1298 reflections with $I > 2\sigma(I)$
R_{int} = 0.072
$\theta_{\max}$ = 30.0°
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -19 \rightarrow 19$
3 standard reflections
frequency: 500 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.056
S = 1.06
1516 reflections
110 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0326P)^2 + 1.2615P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 2.70 e Å^{-3}
$\Delta\rho_{\min}$ = −2.92 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0125 (3)

Table 1
Selected geometric parameters (Å, °).

Hg—O2	2.225 (3)	B2—O1^{iv}	1.347 (5)
Hg—O5^{i}	2.230 (3)	B2—O4	1.379 (5)
Hg—O6^{ii}	2.237 (3)	B2—O5	1.393 (5)
Hg—O4^{iii}	2.240 (3)	B3—O1^{iii}	1.435 (5)
Hg—O3^{iii}	2.793 (3)	B3—O7	1.447 (6)
Hg—O3^{ii}	2.808 (3)	B3—O2	1.499 (5)
Hg—O1	2.989 (3)	B3—O5	1.533 (5)
B1—O3	1.435 (5)	B4—O7	1.347 (5)
B1—O2	1.449 (5)	B4—O3^{v}	1.363 (6)
B1—O6	1.477 (5)	B4—O6	1.395 (5)
B1—O4	1.515 (6)		
O3—B1—O2	120.0 (4)	O1^{iii}—B3—O7	111.9 (4)
O3—B1—O6	106.1 (3)	O1^{iii}—B3—O2	108.8 (3)
O2—B1—O6	108.7 (3)	O7—B3—O2	110.4 (3)
O3—B1—O4	105.3 (3)	O1^{iii}—B3—O5	111.7 (3)
O2—B1—O4	107.9 (3)	O7—B3—O5	107.7 (3)
O6—B1—O4	108.3 (3)	O2—B3—O5	106.2 (3)
O1^{iv}—B2—O4	124.6 (4)	O7—B4—O3^{v}	121.1 (4)
O1^{iv}—B2—O5	117.9 (4)	O7—B4—O6	119.6 (4)
O4—B2—O5	117.5 (4)	O3^{v}—B4—O6	119.3 (4)

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

The crystal structure was refined with the atomic coordinates of the isotypic cadmium compound CdB_4O_7 (Ihara & Krogh-Moe, 1966) as starting parameters. The highest difference peak is located at a distance of 0.74 Å from Hg and the deepest hole 0.72 Å from the same atom.

Data collection: *CAD*-4 *Software* (Enraf—Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *HELENA* implemented in *PLATON* (Spek, 2002); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *SHELXL*97.

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