Refinement of the crystal structure of trimercury(II) orthoborate, $Hg_3(BO_3)_2$

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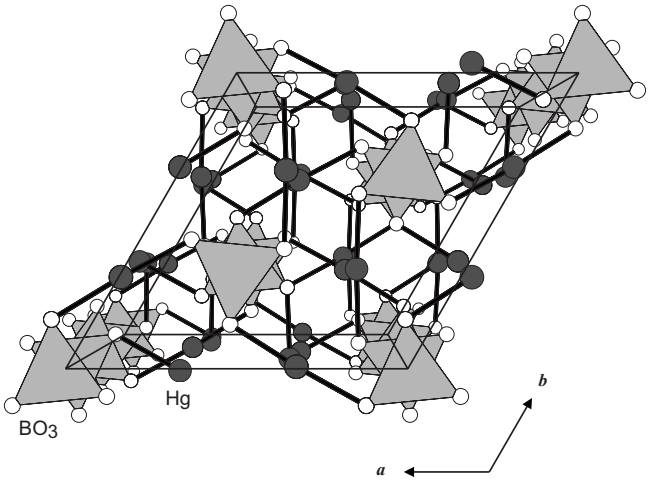

Abstract

$B_2Hg_3O_6$, trigonal, $R\bar{3}c$ (No. 167), a = 8.8936(9) Å, c = 13.052(3) Å, V = 894.1 Å^3, Z = 6, $R_{gt}(F)$ = 0.021, $wR_{ref}(F^2)$ = 0.053, T = 293 K.

Source of material

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 two days which yielded a light-orange polycrystalline product. Application of a temperature gradient 773 K → 723 K for two days led to the formation of colourless single crystals with mostly pinacoidal habit and a length of up to 2 mm at the colder zone of the tube.

Discussion

$Hg_3(BO_3)_2$ has been structurally determined in a previous work by Rietveld refinement of X-ray powder data [1], using the structure of the isotypic $Eu_3(BO_3)_2$ [2] as a starting model. $Ca_3(BO_3)_2$ is another member of this structural family [3,4]. Hg(II) compounds normally show a unique crystal chemistry with a pronounced linear coordination [5,6] of the metal atom in comparison with e.g. the given Eu and Ca compounds . Since the previous model determined by the Rietveld refinement reveals an eight-fold coordinate Hg atom with more or less similar Hg—O distances, it seemed reasonable to refine the structure with higher accuracy on the basis of single crystal data.

$Hg_3(BO_3)_2$ is composed of columns of mercury atoms extended parallel to [001] and which are almost coincident with the 3_1 axis. The nearly planar borate anions are situated on trigonal prismatic holes around the threefold axes and are linked with the metal atoms via short Hg—O distances, as emphasized by the bold sticks in the figure. In contrast to the previous model, Hg shows the expected linear coordination with two very short Hg—O distances of 2.033(4) Å and an ∠O–Hg–O angle of 176.6(2)°. The two next nearest O atoms show significantly longer distances of 2.675(4) Å; the coordination around the Hg atom is augmented by four O atoms with long distances of 3.027(4) Å and 3.044 Å. The geometry of the BO_3^{3-} group deviates only slightly from that of an equilateral triangle and lies with a B—O distance of 1.375(4) Å and an ∠O–B–O angle of 119.98(2)° within the scope of the expected values [7].

Table 1. Data collection and handling.

Crystal:	colourless pinacoid, size 0.22 × 0.33 × 0.38 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	770.51 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, ω
$2\theta_{max}$:	60.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3135, 309
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 307
$N(param)_{refined}$:	19
Programs:	SHELXL-97 [8], HABITUS [9], ATOMS [10]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg	18*e*	0.35247(5)	0	1/4	0.0117(2)	0.0101(2)	0.0184(2)	$U_{22}/2$	0.00037(4)	$2U_{13}$
B	12*c*	0	0	0.3873(6)	0.009(2)	U_{11}	0.012(3)	$U_{11}/2$	0	0
O	36*f*	0.1776(5)	0.0738(5)	0.1111(3)	0.010(2)	0.010(2)	0.027(2)	0.005(2)	–0.003(1)	0.002(1)

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