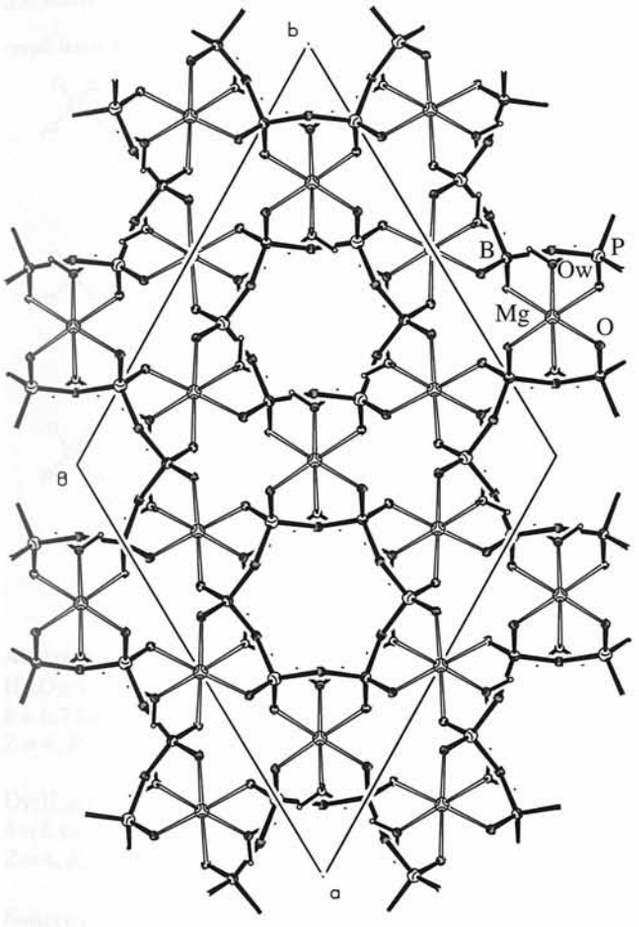
Z. Kristallogr. NCS **218** (2003) 21–22

Crystal structure of diaquamagnesium (dihydrogenmonoborate-monophosphate), $Mg[BPO_4(OH)_2](H_2O)_2$, *containing isolated six-membered rings of tetrahedra*

H.-Z. Shi[I], Y.-K. Shan*[,II], M.-Y. He[II] and Y.-Y. Liu[I]

[I] East China Normal University, Laboratory for Quantum Optics of National Education Ministry, Department of Chemistry, Shanghai 200062, P. R. China
[II] East China Normal University, Department of Chemistry, Shanghai 200062, P. R. China

Received January 9, 2003, accepted and available on-line January 27, 2003; CSD-No. 412922



Abstract

BH_6MgO_8P, trigonal, $R\bar{3}c$ (No. 167), $a = 14.9518(9)$ Å, $c = 13.809(2)$ Å, $V = 2673.6$ Å^3, $Z = 18$, $R_{gt}(F) = 0.030$, $wR_{ref}(F^2) = 0.086$, $T = 293$ K.

Source of material

A mixture of $MgCl_2 \cdot 6H_2O$, H_3PO_4 (85 wt%), H_3BO_3, C_5H_5N, $NH_2NHCSNH_2$ and H_2O in molar ratio of 1 : 1.5 : 8 : 2.5: 1: 22. was loaded in a sealed thick wall Pyrex tube and then placed in an oven at 383 K for 6 days. Colorless cubic crystals were obtained after washing with deionized water. The TG curve showed a two step mass loss of 27.3% (calc. 27 % for a total loss of nine water molecules per formula unit) accompanied by two endothermic DTA peaks (onset: 390 K, peak maximum: 419 K; onset: 478 K, peak maximum: 514 K, respectively).

* Correspondence author (e-mail: ykshan@chem.ecnu.edu.cn)

Discussion

The structure of $Mg[BPO_4(OH)_2](H_2O)_2$, consists of B and P tetrahedra and Mg octahedra. The fundamental unit can be regard as $MgO_2(OH)_2(H_2O)_2$ octahedra linking unbranched six-membered rings $[B_3P_3O_{12}(OH)_6]^{6-}$ of alternating corner sharing $BO_2(OH)_2$ and PO_4 tetrahedra (see figure). These units are repeated along c axis with H bonds spanning the space between units. The coordination octahedra $MgO_2[(OH)_2(H_2O)_2]$ are formed by two protonated B–O3 groups, two P–O1 groups from two adjacent six-membered rings and two H_2O ligands. The Mg octahedron has bonds ranging from d(Mg—O) = 2.024(1) Å to 2.099(1) Å with an average of 2.050 Å. The mean distances $\bar{d}$(P—O) = 1.530 Å and $\bar{d}$(B—O) = 1.470 Å are consistent with those for seamanite ($\bar{d}$(P—O) = 1.534 Å, $\bar{d}$(B—O) = 1.466 Å) [1].

The title structure is very similar to the structure of mineral dioptase $Cu_6[Si_6O_{18}] \cdot 6H_2O$ [2]. The main difference is the number of cations (6 vs. 12) per ring unit $(B_3P_3O_{12}(OH)_6]^{6-}$ vs. $[Si_6O_{18}]^{12-}$). Also, the crystallographic c-axis length of the title compound is approximately doubled compared to that of dioptase. The present synthesis of the nickel-free magnesium borophosphate hydrate validates the deduction made in [3].

Table 1. Data collection and handling.

Crystal:	colorless fragment, size 0.23 × 0.25 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.68 cm^{-1}
Diffractometer, scan mode:	Brucker SMART CCD, φ/ω
$2\theta_{max}$:	54.1°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4855, 665
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 649
$N(param)_{refined}$:	52
Programs:	SHELXTL [4], SHELXL-97 [5]

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

Atom	Site	x	y	z	U_{iso}
H(1)	36*f*	0.008(2)	0.292(2)	0.168(2)	0.025
H(2W)	36*f*	0.172(2)	0.051(2)	0.009(2)	0.025
H(3W)	36*f*	0.223(2)	0.116(2)	0.062(2)	0.025

Table 3. 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}
Mg	18*e*	0.49740(5)	0	1/4	0.0102(3)	0.0115(4)	0.0099(4)	$U_{22}/2$	0.0011(1)	$2U_{13}$
B	18*e*	0.1893(2)	0	1/4	0.0106(8)	0.009(1)	0.010(1)	$U_{22}/2$	–0.0004(4)	$2U_{13}$
P	18*e*	0.81148(4)	0	1/4	0.0093(3)	0.0076(3)	0.0081(3)	$U_{22}/2$	–0.00034(9)	$2U_{13}$
O(1)	36*f*	0.03790(9)	0.26338(9)	0.17022(9)	0.0129(6)	0.0146(6)	0.0136(6)	0.0093(5)	0.0033(4)	0.0046(4)
O(2)	36*f*	0.22693(9)	0.26132(9)	0.16481(9)	0.0117(6)	0.0179(6)	0.0142(6)	0.0084(5)	0.0028(4)	0.0066(4)
O(3)	36*f*	0.2065(1)	0.1027(1)	0.0112(1)	0.0203(7)	0.0152(6)	0.0139(6)	0.0078(5)	0.0010(5)	–0.0003(5)
O(4)	36*f*	0.1733(1)	0.08390(9)	0.21350(9)	0.0297(7)	0.0143(6)	0.0165(7)	0.0153(5)	–0.0105(5)	–0.0056(5)

Acknowledgments. We thank the National Nature Science Foundation (No. 20173017) and the State Key basic program of China (No. G2000048) for the financial support.

References

1. Moor, P.-B.; Ghose, S.: Anovel face-sharing octahedral trimer in the crystal structure of seamanite. Am. Mineral. **56** (1971) 1527-1538.
2. Ribbe, P. -H; Gibbs, G. -V.; Hamil, M.: A refinement of the structure of dioptase, $Cu_6[Si_6O_{18}] \cdot 6H_2O$. Am. Mineral. **62** (1977) 807-811.
3. Boy, I.; Schäfer, G.; Kniep, R.: $(Ni_{3-x}Mg_x)[B_3P_3O_{12}(OH)_6] \cdot 6H_2O$ ($x \approx 1.5$): A novel borophosphate-hydrate containing isolated six-membered rings of tetrahedra. Z. Anorg. Allg. Chem. **627** (2001) 139-143.
4. Bruker SHELXTL. Structure Determination Programs. Version 5.1, Bruker AXS, Inc., Madison, Wisconsin, USA 1997.
5. Sheldrick, G. M.: SHELXL-97. A Program for Refining Crystal Structures. University of Göttingen, Germany 1997.