

Acta Cryst. (1995). **C51**, 351–352

Triclinic $\text{Mg}_2\text{B}_2\text{O}_5$

GUO-CONG GUO, WEN-DAN CHENG, JIU-TONG CHEN,
JIN-SHUN HUANG AND QIAN-ER ZHANG

*State Key Laboratory of Structural Chemistry, Fujian
Institute of Research on the Structure of Matter, CAS,
Fuzhou, Fujian 350002, People's Republic of China*

(Received 14 February 1994; accepted 9 August 1994)

Abstract

The crystal structure of triclinic magnesium pyroborate has been determined. The structure consists of *trans*-edge-shared Mg octahedral tetramer $[\text{Mg}_4\text{O}_{18}]$ chains held together by B atoms which form B_2O_5 (double-triangle) groups. In the Mg octahedral polymer $[\text{Mg}_4\text{O}_{18}]$, the Mg···Mg distances are 3.175 (2) and 3.131 (2) Å.

Comment

Oxide systems containing B_2O_3 have been studied extensively (Sastry & Hummel, 1958; Fletcher, Stevenson & Whitaker, 1970; Mutluer & Timucin, 1975). In the

$\text{MgO-B}_2\text{O}_3$ system, Davis & Knight (1945) reported three binary compounds: $2\text{MgO}\cdot\text{B}_2\text{O}_3$, $\text{MgO}\cdot\text{B}_2\text{O}_3$ and $3\text{MgO}\cdot\text{B}_2\text{O}_3$. Subsequently, Kuzel (1964) reported that $\text{MgO}\cdot\text{B}_2\text{O}_3$ does not exist but that $\text{MgO}\cdot 2\text{B}_2\text{O}_3$ does. Takeuchi (1952) studied the crystal structure of monoclinic magnesium pyroborate ($2\text{MgO}\cdot\text{B}_2\text{O}_3$) using rotation and Weissenberg photographs by the trial-and-error and Fourier series methods. Mrose & Fleischer (1963) studied and compared X-ray diffraction data of monoclinic and triclinic forms of $\text{Mg}_2\text{B}_2\text{O}_5$. Here we report the structure determination of triclinic magnesium pyroborate. The single-crystal structure of the monoclinic form of $\text{Mg}_2\text{B}_2\text{O}_5$ will be reported elsewhere. The triclinic and monoclinic forms of $\text{Mg}_2\text{B}_2\text{O}_5$ are heteromorphic.

The structure of $\text{Mg}_2\text{B}_2\text{O}_5$ is illustrated in Fig. 1. The structure of the title compound is based on $[\text{Mg}_4\text{O}_{18}]$ tetramers, composed of four octahedra linked by three shared edges, connected, through sharing four O–O edges, into chains extended along (001). The B atoms hold the chains together and form B_2O_5 (double-triangle) groups. The Mg···Mg distances of the tetramer $[\text{Mg}_4\text{O}_{18}]$ are 3.175 (2) and 3.131 (2) Å. The O atoms of the B_2O_5 group are not quite coplanar; the dihedral angle between the two slanting trigonal planar BO_3 groups is 9.84° .

Experimental

The compound was obtained by solid-state reaction of the appropriate amounts of H_3BO_3 (chemically pure) and $\text{Mg}_2(\text{OH})_2\text{CO}_3$ (analytical reagent). The reaction was carried out at 1473 K for 5 h, quickly quenched to 1273 K and slowly cooled to 1223 K at a programmed rate of 0.26 K h^{-1} , and air quenched. Crystals of the triclinic form of $\text{Mg}_2\text{B}_2\text{O}_5$ were obtained. The crystals of the monoclinic form of $\text{Mg}_2\text{B}_2\text{O}_5$ were found by slowly cooling from 1093 to 1053 K at a programmed rate of 0.56 K h^{-1} . The single-crystal structure of this compound will be reported elsewhere.

Crystal data

$\text{Mg}_2\text{B}_2\text{O}_5$
 $M_r = 150.23$
Triclinic
 $P\bar{1}$
 $a = 6.149 (3) \text{ \AA}$
 $b = 9.221 (8) \text{ \AA}$
 $c = 3.121 (1) \text{ \AA}$
 $\alpha = 90.29 (5)^\circ$
 $\beta = 92.23 (4)^\circ$
 $\gamma = 104.30 (5)^\circ$
 $V = 171.4 (2) \text{ \AA}^3$
 $Z = 2$
 $D_x = 2.91 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71069 \text{ \AA}$
Cell parameters from 20
reflections
 $\theta = 10\text{--}25^\circ$
 $\mu = 0.567 \text{ mm}^{-1}$
 $T = 296 \text{ K}$
Rectangular
 $0.3 \times 0.1 \times 0.1 \text{ mm}$
White

Data collection

Rigaku AFC-5R diffractometer

$R_{\text{int}} = 0.043$
 $\theta_{\text{max}} = 40^\circ$

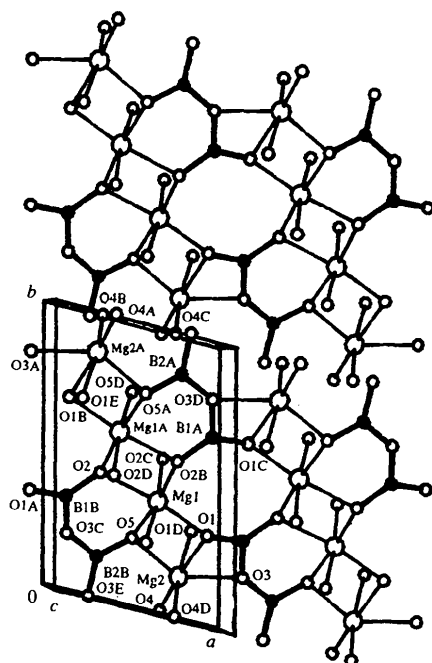


Fig. 1. The structure of $\text{Mg}_2\text{B}_2\text{O}_5$ projected on (001). The large open circles represent Mg, small open circles O and small black circles B atoms.

ω -2 θ scans
 Absorption correction:
 refined from ΔF
 (DIFABS; Walker &
 Stuart, 1983)
 2276 measured reflections
 2133 independent reflections
 1944 observed reflections
 $[I > 3\sigma(I)]$

$h = 0 \rightarrow 11$
 $k = -17 \rightarrow 17$
 $l = -6 \rightarrow 6$
 3 standard reflections
 monitored every 250
 reflections
 intensity decay: 1.0%

O(2ⁱ)—Mg(1)—O(5) 173.75 (4) O(4ⁱⁱⁱ)—Mg(2)—O(4) 102.71 (6)
 O(2^j)—Mg(1)—O(5ⁱⁱⁱ) 84.13 (6) O(4)—Mg(2)—O(5) 103.83 (5)
 O(5ⁱⁱⁱ)—Mg(1)—O(2) 90.52 (5) O(4ⁱⁱⁱ)—Mg(2)—O(5) 102.44 (5)
 O(5)—Mg(1)—O(2ⁱⁱ) 83.36 (6) O(5)—Mg(2)—O(1) 79.92 (5)
 O(5)—Mg(1)—O(2) 89.60 (5) O(5)—Mg(2)—O(1^{iv}) 80.93 (5)
 O(5)—Mg(1)—O(5ⁱⁱⁱ) 95.33 (6) O(5)—Mg(2)—O(3) 139.36 (5)
 O(1)—B(1)—O(2ⁱⁱⁱ) 128.86 (8) O(4)—B(2)—O(5^{vii}) 124.82 (8)
 O(1)—B(1)—O(3) 110.94 (8) O(4)—B(2)—O(3^{vi}) 116.82 (8)
 O(2^{viii})—B(1)—O(3) 120.19 (8) O(5^{vii})—B(2)—O(3^{vi}) 118.35 (8)

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, 1 - y, -z$;
 (iii) $x, y, 1 + z$; (iv) $x, y, z - 1$; (v) $x - 1, y, z$; (vi) $2 - x, -y, -1 - z$;
 (vii) $1 - x, -y, -1 - z$; (viii) $1 + x, y, z$.

Refinement

Refinement on F
 $R = 0.030$
 $wR = 0.047$
 $S = 1.55$
 1944 reflections
 82 parameters
 $w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.0008$
 $\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.52 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors
 from Cromer & Waber
 (1974)

The structure was solved by direct methods (Gilmore, 1983) and difference Fourier techniques, and refined by a full-matrix least-squares method (Peterse & Palmy, 1966). All calculations were performed on a VAX 11/785 computer using TEXSAN (Molecular Structure Corporation, 1985).

This work was supported financially by the National Science Foundation of China, the State Key Laboratory of Structural Chemistry and the Nature Science Foundation of Fujian Province. We would like to thank the referee for a beneficial comment on this paper.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq}
Mg(1)	0.62787 (5)	0.39744 (3)	0.26628 (8)	0.434 (8)
Mg(2)	0.78956 (5)	0.14432 (3)	-0.23131 (9)	0.488 (8)
O(1)	0.90678 (9)	0.31943 (6)	0.2782 (2)	0.54 (1)
O(2)	0.30443 (9)	0.44687 (6)	0.2347 (2)	0.46 (1)
O(3)	1.13818 (9)	0.19985 (6)	-0.0619 (2)	0.60 (1)
O(4)	0.7247 (1)	0.00497 (6)	-0.7297 (2)	0.57 (1)
O(5)	0.52277 (9)	0.24165 (6)	-0.2424 (2)	0.48 (1)
B(1)	1.1204 (1)	0.33098 (8)	0.1655 (2)	0.43 (2)
B(2)	0.6818 (1)	-0.14330 (8)	-0.8007 (2)	0.44 (2)

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1079). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. Selected geometric parameters (\AA , $^\circ$)

Mg(1)···Mg(2)	3.175 (2)	Mg(2)—O(3)	2.122 (1)
Mg(1)···Mg(1 ⁱ)	3.131 (2)	Mg(2)—O(4)	1.977 (1)
Mg(1)—O(1)	2.016 (1)	Mg(2)—O(4 ⁱⁱⁱ)	2.019 (1)
Mg(1)—O(2 ⁱ)	2.072 (1)	Mg(2)—O(5)	2.055 (1)
Mg(1)—O(2 ⁱⁱ)	2.111 (2)	O(1)—B(1)	1.352 (1)
Mg(1)—O(2)	2.146 (1)	O(2)—B(1 ^v)	1.360 (1)
Mg(1)—O(5)	2.108 (2)	O(3)—B(1)	1.428 (1)
Mg(1)—O(5 ⁱⁱⁱ)	2.115 (2)	O(3)—B(2 ^{vi})	1.415 (1)
Mg(2)—O(1)	2.229 (2)	O(4)—B(2)	1.342 (2)
Mg(2)—O(1 ^{iv})	2.238 (2)	O(5)—B(2 ^{vii})	1.369 (1)
O(1)—Mg(1)—O(2 ⁱ)	102.36 (5)	O(1 ^{iv})—Mg(2)—O(1)	88.67 (6)
O(1)—Mg(1)—O(2 ⁱⁱ)	101.01 (5)	O(3)—Mg(2)—O(1)	63.49 (5)
O(1)—Mg(1)—O(2)	171.54 (3)	O(3)—Mg(2)—O(1 ^{iv})	81.16 (5)
O(1)—Mg(1)—O(5)	83.78 (5)	O(4 ⁱⁱⁱ)—Mg(2)—O(1)	83.70 (6)
O(1)—Mg(1)—O(5 ⁱⁱⁱ)	84.89 (5)	O(4 ⁱⁱⁱ)—Mg(2)—O(1 ^{iv})	170.94 (3)
O(2)—Mg(1)—O(2 ⁱⁱ)	83.37 (5)	O(4)—Mg(2)—O(1)	171.49 (3)
O(2 ⁱⁱ)—Mg(1)—O(2 ⁱ)	96.51 (6)	O(4)—Mg(2)—O(1 ^{iv})	84.43 (6)
O(2)—Mg(1)—O(2 ⁱ)	84.18 (5)	O(4)—Mg(2)—O(3)	110.35 (5)
O(2 ⁱⁱ)—Mg(1)—O(5 ⁱⁱⁱ)	173.74 (3)	O(4 ⁱⁱⁱ)—Mg(2)—O(3)	91.03 (5)

METAL-ORGANIC COMPOUNDS

Acta Cryst. (1995), **C51**, 353–356

Hydrogen-Bonded Self-Assembly of Tris(2-ammonioethyl)amine Molybdate Hydrate, $4[\text{N}(\text{CH}_2\text{CH}_2\text{NH}_3)_3]^{3+} \cdot 6[\text{MoO}_4]^{2-} \cdot 6\text{H}_2\text{O}$

ELMER C. ALYEA, GEORGE FERGUSON AND ZHENG XU†

*Department of Chemistry and Biochemistry,
University of Guelph, Guelph, Ontario,
Canada N1G 2W1*

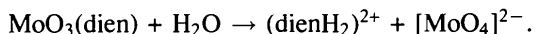
(Received 26 July 1994; accepted 1 September 1994)

Abstract

The title compound consists of a three-dimensional network of cations, anions and water molecules linked through hydrogen bonding in which all available hydrogen-bond donors are utilized. In four of the tetrahedral $[\text{MoO}_4]^{2-}$ anions, one O atom is hydrogen bonded with the three protonated groups of a cation. The other O atoms in these four $[\text{MoO}_4]^{2-}$ anions and those of the remaining two $[\text{MoO}_4]^{2-}$ anions are all involved as acceptors in either $\text{O}—\text{H} \cdots \text{O}$ [2.713 (4)–2.865 (4) Å] or $\text{N}—\text{H} \cdots \text{O}$ [2.656 (5)–2.989 (4) Å] hydrogen bonds with water molecules or adjacent cations. The mean Mo—O distance increases with the number of hydrogen bonds for which the O atom acts as an acceptor [1.728 (10), 1.758 (6) and 1.774 (8) Å for one, two and three hydrogen bonds, respectively].

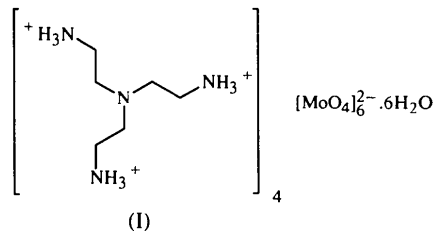
Comment

The transformation of molybdenum trioxide in aqueous solution to the more soluble $[\text{MoO}_4]^{2-}$ anion is of interest because the latter form is that in which the molybdenum is subsequently incorporated into essential molybdo-enzyme systems from its natural aqueous environment (Stiefel, 1977). In an earlier study of the interaction of solid MoO_3 with polydentate amines, the reaction product with diethylenetriamine (dien) was formulated as the neutral adduct $\text{MoO}_3(\text{dien})$ (Marzluff, 1964); the *fac*-octahedral geometry, with $\text{N}—\text{Mo}—\text{N}$ 75° (average) and $\text{O}—\text{Mo}—\text{O}$ 106° (average), was confirmed by X-ray analysis (Cotton & Elder, 1964). Later work (Taylor, Gans, Knowles & Sykes, 1974) indicated that $\text{MoO}_3(\text{dien})$ undergoes extensive protonation in aqueous solution:



† Permanent address: Chemistry Department, Nanjing University, Nanjing 210093, People's Republic of China.

We now report that tris(2-aminoethyl)amine (tren), a potentially tetradentate amine, undergoes hydrogen-bonded self-assembly with solid MoO_3 in aqueous solution to form $(\text{trenH}_3)_4^{3+} \cdot 6[\text{MoO}_4]^{2-} \cdot 6\text{H}_2\text{O}$, (I).



Although formed even when a 1:1 ratio of tren:MoO₃ is employed, the colourless ionic solid is produced in greatest yield (89%) when the tren:MoO₃ ratio is 2:3. Strong hydrogen bonding within the compound is indicated by the presence of an intense broad infrared band due to $\nu(\text{O}—\text{H})$ and $\nu(\text{N}—\text{H})$ (in the range 3400–2100 cm^{-1}) and displacement of the strong $\nu(\text{Mo}=\text{O})$ peak to 810 cm^{-1} (from 940 cm^{-1} in $[\text{MoO}_4]^{2-}$). ¹H NMR spectroscopy in D₂O shows a singlet at δ 4.73 p.p.m., assigned to HDO produced by exchange, and triplets at δ 3.08 and 2.75 p.p.m., assigned to the methylene protons; the ¹H NMR peaks observed for tren itself in D₂O occur at δ 4.78, 2.65 and 2.49 p.p.m. These data did not allow us to distinguish between ionic and neutral formulations of the product.

The crystal structure analysis shows that the solid material contains protonated $(\text{trenH}_3)^{3+}$ cations, tetrahedral $[\text{MoO}_4]^{2-}$ anions and water molecules in a 4:6:6 ratio in the asymmetric unit; these moieties are all linked by an extensive three-dimensional hydrogen-bonded network which utilizes all available hydrogen bond donors. All H atoms in the asymmetric unit were clearly visible in difference maps and were allowed for as riding atoms.

There are four distinct cation–anion hydrogen-bonded pairs in the asymmetric unit of (I); one of these is shown in Fig. 1. In each of these, one O atom ($\text{O}i1$, $i = 1–4$) is hydrogen bonded with the three protonated groups of a $(\text{trenH}_3)^{3+}$ cation [$\text{N}(\text{H}) \cdots \text{O}$ 2.739 (4)–2.832 (4) Å]; the mean non-bonding distance between such an O atom and the central N of the cation to which it is triply hydrogen-bonded is 3.27 (4) Å. The other O atoms in these four $[\text{MoO}_4]^{2-}$ anions and those of the remaining two $[\text{MoO}_4]^{2-}$ anions are all involved as acceptors in either $\text{O}—\text{H} \cdots \text{O}$ [2.713 (4)–2.865 (4) Å] or $\text{N}—\text{H} \cdots \text{O}$ [2.656 (5)–2.989 (4) Å] hydrogen bonds with water molecules or adjacent $(\text{trenH}_3)^{3+}$ cations. The hydrogen-bonding pattern is completed by additional $\text{O}—\text{H} \cdots \text{O}$ hydrogen bonds between water molecules [$\text{O} \cdots \text{O}$ 2.834 (4)–2.947 (5) Å].