

*Acta Cryst.* (1963). **16**, 849

**New transition metal borates with the calcite structure.** By I. BERNAL, C. W. STRUCK and J. G. WHITE, *RCA Laboratories, Princeton, New Jersey, U.S.A.*

(Received 25 September 1962 and in revised form 14 March 1963)

Certain metal orthoborates have been known for many years to be isostructural with different forms of calcium carbonate. Thus scandium and indium borates form the calcite structure and yttrium borate the aragonite structure (Goldsmith & Hauptmann, 1932). Lanthanum borate also is reported to crystallize in the aragonite structure (Keith & Roy, 1954).

X-ray data were obtained from both powder patterns and single-crystal Weissenberg photographs using Mn-filtered Fe  $K\alpha$  radiation. The unit cell is rhombohedral with  $a_r = 5.496 \text{ \AA}$ ,  $\alpha = 49^\circ 38'$  or  $a_h = 4.613 \pm 0.005 \text{ \AA}$ ,  $c_h = 14.42 \pm 0.01 \text{ \AA}$  referred to the triply primitive hexagonal cell. The systematic absence of  $h0l$  reflections with  $l$  odd limited the space group to  $R\bar{3}c$  or  $R3c$ . Inten-

Table 1. *Magnetic moments of borates*  
( $\text{Fe}_{1-x}\text{M}_x\text{BO}_3$ )

Composition	Chemical analysis*	Magnetic moment† at 293 °K ( $\mu_B \cdot \text{mole}^{-1}$ )	Magnetic moment† at 77 °K ( $\mu_B \cdot \text{mole}^{-1}$ )
$\text{FeBO}_3$	$\text{Fe}_{0.97}\text{B}$	$4.5 \times 10^{-2}$	—
$\text{Fe}_{0.9}\text{Ga}_{0.1}\text{BO}_3$	$\text{Fe}_{0.93}\text{Ga}_{0.1}\text{B}$	—	—
$\text{Fe}_{0.8}\text{Ga}_{0.2}\text{BO}_3$	$\text{Fe}_{0.86}\text{Ga}_{0.15}\text{B}$	$1.04 \times 10^{-2}$	$4.91 \times 10^{-2}$
$\text{Fe}_{0.6}\text{Ga}_{0.4}\text{BO}_3$	$\text{Fe}_{0.6}\text{Ga}_{0.25}\text{B}$	$0.946 \times 10^{-2}$	$5.55 \times 10^{-2}$
$\text{Fe}_{0.2}\text{Ga}_{0.8}\text{BO}_3$	$\text{Fe}_{0.21}\text{Ga}_{0.78}\text{B}$	$0.408 \times 10^{-2}$	$0.905 \times 10^{-2}$
$\text{Fe}_{0.8}\text{Cr}_{0.2}\text{BO}_3$	$\text{Fe}_{0.92}\text{Cr}_{0.12}\text{B}$	$3.25 \times 10^{-2}$	$5.32 \times 10^{-2}$
$\text{Fe}_{0.9}\text{Ti}_{0.1}\text{BO}_3$	$\text{Fe}_{0.9}\text{Ti}_{0.1}\text{B}$	$3.06 \times 10^{-2}$	$2.85 \times 10^{-2}$

\* The amounts of metal ions present relative to boron are given. No oxygen determination was performed.

† Magnetic moment for an applied field of 10,000 oersteds.

In the course of our investigations on magnetic oxide systems, we have found a new family of compounds with the calcite structure. These materials are borates of iron which can be described by the general formula



where M is a metal. The metals that we have successfully introduced in this structure are shown in Table 1. None of the compounds described could be prepared by standard powder techniques.

All of these materials were prepared as powders from a  $\text{Bi}_2\text{O}_3$ - $\text{B}_2\text{O}_3$  flux, using the mole ratio  $\text{M}_2\text{O}_3:\text{Bi}_2\text{O}_3:\text{B}_2\text{O}_3$  of 1:1:5. After fusion at about 1200 °C, the melt was annealed for several days at 900 °C. Since without such an annealing procedure one obtains only the oxide phase, it is probable that the borates decompose into their component oxides somewhere between these two temperatures.

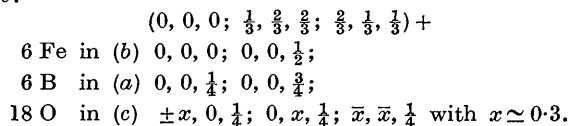
The crystallographic determination of structure and parameters was carried out in a crystal of composition  $\text{Fe}_{0.9}\text{Ga}_{0.1}\text{BO}_3$  that was grown as follows: 82.8 g  $\text{B}_2\text{O}_3$ , 139.8 g  $\text{Bi}_2\text{O}_3$ , 27.24 g  $\text{Fe}_2\text{O}_3$ , 16.08 g  $\text{Ga}_2\text{O}_3$  were mixed in a ball mill. The mixture was placed in a 200 ml platinum crucible and melted with a Meker burner and placed in an oven. The temperature was raised to 1145 °C and cooled at the rate of 1.1 °C per hr for 12 days. This slow rate of cooling effectively included the annealing process described above. The crucible and contents were then quenched to room temperature and placed in a beaker of boiling 6N  $\text{HNO}_3$ . After some hours, crystals separated from the surrounding flux. These were yellowish green well-formed hexagonal plates, several millimetres in diameter.

Table 2. *Observed and calculated lattice spacings and intensities for  $\text{Fe}_{0.9}\text{Ga}_{0.1}\text{BO}_3$ .*

Indices refer to the triply primitive hexagonal cell

$hkl$	$d_o$	$d_c$	$I_o$	$I_c \times 10^{-4}$
102	3.491	3.494	59	66
104	2.673	2.676	118	117
110	2.302	2.307	19	21
113	2.076	2.079	30	32
202	1.923	1.925	25	26
204	1.745	1.747	16	13
116	1.662	1.664	42	42
108	1.641	1.643	26	21
212	1.477	1.478	16	17
214	1.391	1.393	17	15
10,10	1.355	1.356	6	4
208	1.336	1.338	7	6
300	1.331	1.332	17	21
119	1.316	1.316	6	5
00,12	1.201	1.202	8	7
20,10	1.169	1.169	6	6
218	1.158	1.157	12	13
223	1.121	1.121	3	2
312	1.095	1.095	5	5
11,12	1.066	1.066	11	10
314	1.058	1.059	23	28
21,10	1.043	1.043	14	15
226	1.040	1.040	23	21
10,14	0.997	0.997	8	6

sities were estimated visually from an X-ray powder pattern using a multiple film technique and the line at  $x=0, y=0$  and the section at  $z=\frac{1}{2}$  of the three-dimensional Patterson function were computed. All the peaks and their relative heights could be accounted for by placing the atoms in the following positions of the space group  $R\bar{3}c$ :



This is the calcite structure type  $G1$  (*Strukturbericht*, 1931). The other metal atoms are substituted randomly in the iron positions. The oxygen parameter was adjusted to give the best agreement with the observed data which was found with  $x=0.290$  corresponding to a B-O distance of 1.34 Å. The measured and calculated values of the lattice spacings and intensities are listed in Table 2. The scattering factors used are those given in *Internationale Tabellen* (1935) corrected for anomalous dispersion (Dauben & Templeton, 1955). Direct comparison of the

X-ray powder photographs of the other preparations showed no change in the lattice constants throughout.

The magnetic moments listed in Table 1 were obtained with a vibrating sample magnetometer by P. K. Baltzer and S. Kasdan. These results are difficult to interpret since it is not obvious what the type and strength of the interaction of magnetic ions in this structure might be. Moments of this magnitude could conceivably be accounted for by the presence of small amounts of ferrimagnetic impurities (*e.g.*  $\text{Fe}_3\text{O}_4$ ), although no such phases have been observed in the X-ray patterns.

We thank R. E. Nielsen for the chemical preparations, K. L. Cheng and H. H. Whitaker for chemical analyses,

L. A. Zandoni and G. W. Neighbor for help in the experimental work, and Mrs D. Garrison for processing the crystallographic computations.

### References

- DAUBEN, C. H. and TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.  
 GOLDSCHMIDT, V. M. & HAUPTMANN, H. (1932). *Nachr. Ges. Wiss. Göttingen*, p. 53.  
 KEITH, M. L. & ROY, R. (1954). *Amer. Min.* **39**, 1.  
*Internationale Tabellen*. (1935). Vol. II. Berlin: Borntraeger.  
*Strukturbericht* (1931). **1**, 292.

*Acta Cryst.* (1963). **16**, 850

### Crystallographic data for the $\alpha$ and $\beta$ isomers of 4-hydroxy-2,2,6-trimethylpiperidine hydrochloride and the $\beta$ -O-benzyl hydrochloride. By J. G. SCANE, *Physics Department, College of Technology, Portsmouth, England*

(Received 20 March 1963)

Data for the  $\alpha$  and  $\beta$  isomers of the free base have already been obtained (Scane, 1961), and it was intended to use the hydrochlorides to establish the configuration and conformation of each isomer. Owing to the small number of reflexions observed for the hydrochlorides they have been dropped in favour of the non-isomorphous hydrobromides.

Doubt exists as to the position of the methyl groups, for although infrared studies have shown the existence of an N-H stretch in piperidine and the ketone from which both isomers are prepared, both the  $\alpha$  and  $\beta$  bases show no sign of the N-H stretch.

#### $\alpha$ -B.HCl (m. p. over 300 °C)

The hydrochloride of the  $\alpha$  isomer was prepared from the ( $\pm$ )base by precipitation from solution by HCl gas and recrystallization from ethanol. Very good colourless crystals were obtained elongated along [100] with (011) and (001) prominent. A full survey of the reciprocal lattice was carried out twice on two separate crystals with a stationary-film single-crystal camera and Cu  $K\alpha$  radiation. The density was measured by flotation in a benzene-bromoform mixture, and analysis confirmed the formula  $\text{C}_8\text{H}_{18}\text{ONCl}$ .

#### $\beta$ -B.HCl (m. p. 191-193 °C)

Crystals of the hydrochloride of the  $\beta$  isomer were prepared and studied in the same way as for the  $\alpha$ -B.HCl. They are colourless tablets with (010) prominent. Analysis confirmed the formula  $\text{C}_8\text{H}_{18}\text{ONCl}\cdot\text{H}_2\text{O}$ , and vacuum desiccation at 80 °C removed the water of crystallization and caused the crystals to disintegrate.

#### $\beta$ -O-benzyl HCl (m. p. 269-271 °C)

The hydrochloride of the  $\beta$  isomer of the O-benzyl

derivative crystallized in well formed plates with (001) prominent. The X-ray investigation was carried out in the same way.

Table 1. *Crystallographic data*

	$\alpha$ -B.HCl	$\beta$ -B.HCl	$\beta$ -O-Benzyl HCl
<i>a</i>	8.7 <sub>0</sub> Å	7.7 <sub>3</sub> Å	10.2 Å
<i>b</i>	9.4 <sub>5</sub> Å	19.6 Å	12.3 Å
<i>c</i>	12.5 Å	8.6° Å	48.4 Å
$\beta$		122°	
<i>D</i> <sub>o</sub>	1.16 g.cm <sup>-3</sup>	1.17 g.cm <sup>-3</sup>	1.23 g.cm <sup>-3</sup>
<i>D</i> <sub>c</sub>	1.16 g.cm <sup>-3</sup>	1.18 g.cm <sup>-3</sup>	1.24 g.cm <sup>-3</sup>
<i>Z</i>	4	4	16
Space group	$P2_12_12_1$	$P2_1/c$	$Fd2d$

Crystallographic data for the three hydrochlorides are given in Table 1. The space groups were determined uniquely from the systematic absences in all cases.

Since  $P2_12_12_1$  requires four identical asymmetric units to the unit cell, the unit cell of the  $\alpha$ -B.HCl cannot contain both + and - molecules. Hence the  $\alpha$ -racemate must separate into the + and - forms on crystallization. This is consistent with the observation that the  $\alpha$  hydrochlorides all melt above 300 °C whether prepared from D, L or DL base (King, 1924). The other two hydrochlorides obviously crystallize as racemates.

I am indebted to Dr F. Perks for the specimens and the analyses, Dr E. M. Bradbury for interpretation of the infrared spectra, and Dr D. Rogers for guidance.

### References

- KING, H. (1924). *J. Chem. Soc.* p. 41.  
 SCANE, J. G. (1961). *Acta Cryst.* **14**, 1005.