

Table 5 (*cont.*)

Zn-tetrahedron		
O(1)-Zn-O(3)		125.3 (3)°
O(3)-O(5)		89.1 (3)
O(5)-O(6)		110.4 (3)
O(6)-O(1)		91.3 (3)
O(1)-O(5)		120.8 (3)
O(3)-O(6)		121.7 (3)

The numerical calculations were carried out on the 7070 IBM computer of the Centro de Cálculo Electrónico del C.S.I.C., Spain, and on the 7090 IBM computer of the Centro de Cálculo de la Universidad de Madrid, Spain. This work forms part of the Ph. D. Thesis of one of us (M.M.R.) who also acknowledges the research grant given by Ministerio de Educación y Ciencia, Spain.

References

- BAUER, H. (1963). *Z. anorg. Chem.* **320**, 306.
BLOCK, S. & PERLOFF, A. (1965). *Acta Cryst.* **19**, 297.

- BUERGER, M. J. (1959). *Vector Space*. New York: John Wiley.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORNL Report TM-305. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. Oxford: Pergamon Press.
FAYOS, J., GARCIA-BLANCO, S. & RIVOIR, L. (1966). *An. R. Soc. Esp. Fis. Quim.* **62A**, 297.
GARCIA-BLANCO, S. & FAYOS, J. (1968). *Z. Kristallogr.* **127**, 145.
HARRISON, D. E. & HUMMEL, F. A. (1956). *J. Electrochem. Soc.* **103**, 491.
IHARA, M. & KROGH-MOE, J. (1966). *Acta Cryst.* **20**, 132.
KROGH-MOE, J. (1968). *Acta Cryst.* **B24**, 179.
MORIMOTO, N. (1956). *Miner. J. (Japan)*, **2**, 1.
PERLOFF, A. & BLOCK, S. (1966). *Acta Cryst.* **20**, 274.
SMITH, P., GARCIA-BLANCO, S. & RIVOIR, L. (1964). *Z. Kristallogr.* **119**, 375.
WEIR, C. E. & SCHROEDER, R. A. (1964). *J. Res. Nat. Bur. Stand.* **68A**, 465.
ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 385.

Acta Cryst. (1971). **B27**, 677

The Crystal Structure of Copper Metaborate, CuB_2O_4

BY M. MARTINEZ-RIPOLL, S. MARTINEZ-CARRERA AND S. GARCIA-BLANCO

Instituto de Química Física Rocasolano, Serrano 119, Madrid-6, Spain

(Received 20 July 1970)

Copper metaborate crystallizes in the tetragonal system, space group $I\bar{4}2d$, with twelve formula units in a cell of dimensions $a = 11.484 \pm 0.004$ and $c = 5.620 \pm 0.004$ Å. The calculated density is 4.02 g.cm^{-3} . The structure of CuB_2O_4 has been determined by three-dimensional Fourier syntheses. The positional and isotropic thermal parameters were refined by least-squares analysis, yielding a final R value of 0.053. All boron atoms are tetrahedrally coordinated. The structure consists of BO_4 tetrahedra sharing the four common oxygen atoms. Each copper atom is surrounded in a planar-square coordination by four oxygen atoms. All interatomic distances are of the usual order of magnitude.

Introduction

The binary system $\text{CuO}-\text{B}_2\text{O}_3$ has been treated by Weir & Schroeder (1964) in a preliminary study. In accordance with their results two copper borates were easily prepared by heating two mixtures of boron and copper oxides. Powder X-ray diffraction patterns of these compounds were taken. One compound apparently corresponds to the formula $3\text{CuO} \cdot \text{B}_2\text{O}_3$, and forms laminar green crystals. The other compound exactly corresponds to the formula $\text{CuO} \cdot \text{B}_2\text{O}_3$, and forms deep blue crystals. The purpose of the present paper is to report on the crystal structure of the phase $\text{CuO} \cdot \text{B}_2\text{O}_3$.

The structures of several anhydrous borates with a metal oxide to boron oxide ratio of 1:1 are known. In some of them, namely NaBO_2 (Marezio, Plettinger & Zachariasen, 1963*a*), $\text{CaB}_2\text{O}_4(\text{I})$ (Marezio, Plettinger

& Zachariasen, 1963*b*), $\text{LiBO}_2(\text{I})$ (Zachariasen, 1964) and BaB_2O_4 (Mighell, Perloff & Block, 1966), all boron atoms have a coordination number 3. On the other hand, in the isomorphous $\text{SrB}_2\text{O}_4(\text{IV})$ (Dernier, 1969) and $\text{CaB}_2\text{O}_4(\text{IV})$ (Marezio, Remeika & Dernier, 1969*b*), and in $\text{LiBO}_2(\text{III})$ (Marezio & Remeika, 1966), all boron atoms are tetrahedrally coordinated. Finally, $\text{CaB}_2\text{O}_4(\text{III})$ (Marezio, Remeika & Dernier, 1969*a*), an isomorph of $\text{SrB}_2\text{O}_4(\text{III})$ (Dernier, 1969), contains BO_3 triangles and BO_4 tetrahedra. As part of a programme in progress aimed at achieving a better understanding of the structural principles of anhydrous borate compounds, the structure of CuB_2O_4 was selected for study.

Experimental

Single crystals of copper metaborate were prepared by annealing a melt of stoichiometry $\text{CuO} \cdot \text{B}_2\text{O}_3$ at

1.000°C. Under these conditions nearly prismatic deep blue crystals were obtained; they are extremely hard and insoluble in acids. Chemical analysis of the Cu and B contents in the crystals led to the formula CuB_2O_4 .

The symmetry, space group and approximate lattice parameters were determined from Weissenberg photographs taken with Cu $K\alpha$ radiation. CuB_2O_4 was found to be tetragonal with twelve molecules per unit cell. The systematic absences correspond to two space groups, $I\bar{4}2d$ and $I4_1md$. Analysis of the (001) Patterson function indicated that the correct space group was $I\bar{4}2d$. Lattice parameters determined from the Weissenberg photographs were used to index the powder pattern. Precise lattice parameters were obtained by accurate measurements of the d values for several reflexions. The following dimensions were found: $a = 11.484 \pm 0.004$ and $c = 5.620 \pm 0.004$ Å. A list of observed interplanar spacings is given in Table 1. The calculated and observed densities are 4.02 and 3.99 g.cm^{-3} respectively.

Table 1. Powder pattern of CuB_2O_4

hkl	d	I	hkl	d	I
200	5.734 Å	15	413	1.554 Å	10
101	5.042	10	622	1.525	10
220	4.060	10	433, 503	1.453	4
211	3.792	100	800	1.435	2
310	3.632	50	523, 712,	1.407	20
301	3.159	15	004, 552		
400	2.873	30	820	1.393	4
321	2.769	45	642	1.386	5
112	2.653	40	741, 811	1.381	10
420	2.567	35	204	1.365	4
202	2.522	25	660	1.354	4
411	2.494	40	732	1.329	6
312	2.222	15	224	1.328	5
431, 501	2.126	15	314, 831	1.308	4
440	2.030	4	802, 840	1.279	4
402	2.008	15	633	1.264	4
521	1.993	4	761, 921	1.217	5
530	1.969	10	723, 752	1.207	6
332	1.949	4	851	1.190	20
600	1.914	6	653, 912	1.157	4
422	1.895	15	743, 813	1.134	5
103	1.848	25	604	1.133	8
620	1.816	25	932	1.112	4
611	1.790	45			
213	1.759	10			
512	1.757	12			
541	1.709	20			
631	1.637	4			
532	1.613	6			
701	1.575	4			

Cu $K\alpha$ radiation and an integration equi-inclination Weissenberg technique were used. The intensity data from five reciprocal layers along the c axis were measured photometrically. For the purpose of the present work absorption corrections were not relevant ($\mu R \approx 1.6$). In any case, such corrections would be tedious because of the irregular form of the crystals.

Structure determination

The first step in the solution of the structure was based on the determination of the positions of the Cu atoms. The analysis of the (001) Patterson function indicated the correct choice of space group to be $I\bar{4}2d$. All major peaks in the Patterson synthesis could be explained by placing Cu(1) at $(0, 0, \frac{1}{2})$ and Cu(2) at $(0.08, \frac{1}{4}, \frac{1}{8})$. Three-dimensional structure factors based on these coordinates, assuming isotropic temperature factors of 1.0 \AA^2 , correspond to $R = 0.320$. The f -curves for neutral Cu, O and B were used. A three-dimensional Fourier synthesis, computed with the phases of the copper atoms, gave the positions of the four oxygen and two boron atoms; the R index was reduced to 0.143. Since the structural arrangement obtained was reasonable from the crystal chemistry point of view, this structure was refined by the use of the least-squares program *ORFLS* (Busing, Martin & Levy, 1962), yielding a final R value of 0.053. Reflexions were given weights according to Hughes (1941) scheme. Since the temperature factors of some oxygen and boron atoms became negative (small values) at the final stage of the refinement, they were fixed at low values and were not varied in the final calculations. Therefore their actual values are not significant. A possible explanation of this may be the existence of some slight absorption effects, in spite of the small size of the crystal. The positional and thermal parameters are shown in Table 2. The observed and calculated structure factors are given in Table 3.

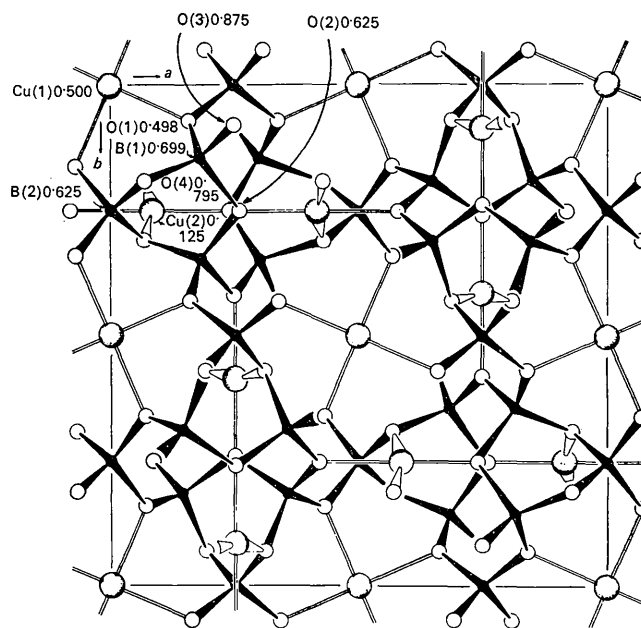


Fig. 1. The projection of one unit cell on (001). The heights of the atoms as fractions of the c parameter are given. Note that a left-handed system of axes has been used.

oxygen separations, together with the four oxygen atoms arranged in planar-square coordination, form a greatly distorted octahedron around $\text{Cu}(2)$, as shown in Fig. 4. This distortion from a regular octahedral coordination is generally explained as being a consequence of the Jahn-Teller effect. In CuB_2O_4 , the deviation from such a coordination is considerable. In this case the elongation of the interatomic distance is 1.13 Å, *i.e.* 58%. Furthermore this elongation does not occur purely along a fourfold axis of the octahedron, but is tilted 29.7° about that direction. A similar result has recently been observed in CuO (Åsbrink & Norrby, 1970), where the distortion from the regular octahedron involves an elongation of 0.82 Å (42%), with tilt of 17° about the fourfold axis of the octahedron. The large separations, $\text{Cu}(2)\text{-O}(1) = 3.069$ Å, are, however, greater than typical separations for the (4+2) coordination and, hence, do not appear to be involved in the coordination around $\text{Cu}(2)$. Therefore all copper atoms have planar-square coordination. The equations for the best least-squares planes calculated by the method of Schomaker, Waser, Marsh & Bergman (1959) are:

for the oxygen atoms coordinated to $\text{Cu}(1)$,

$$z - 2.8100 = 0;$$

for the oxygen atoms coordinated to $\text{Cu}(2)$,

$$0.9353 y - 0.3537 z - 2.4369 = 0.$$

$\text{O}(1)$ is at 0.010 Å from the least-squares plane passing through $\text{Cu}(1)$, and all atoms forming the least-squares plane passing through $\text{Cu}(2)$ are exactly coplanar because of the symmetry. The coordination number of the oxygen atoms is three; each is surrounded by one copper atom and two boron atoms.

All interatomic distances and their standard deviations are reported in Table 4. The individual valence angles O-B-O and O-Cu-O together with their standard deviations are shown in Table 5. The infrared spectra of copper metaborate show strong absorption near 1.100 cm^{-1} . Otherwise, there are no strong bands at higher frequencies (Fig. 5). These results seem to be in good agreement with the existence of BO_4 groups only.

Table 4. *Interatomic distances*

B(1)-tetrahedron			
B(1)-O(1)	1.46 (1) Å	O(1)-O(2)	2.42 (1) Å
-O(2)	1.47 (1)	O(2)-O(3)	2.37 (1)
-O(3)	1.45 (1)	O(3)-O(4)	2.39 (1)
-O(4)	1.44 (1)	O(4)-O(1)	2.36 (1)
Average	1.46	O(1)-O(3)	2.36 (1)
		O(2)-O(4)	2.36 (1)
B(2)-tetrahedron			
B(2)-O(1)	1.48 (1) Å	O(1)-O(1 ¹)	2.50 (1) Å
-O(1 ¹)	1.48 (1)	O(1 ¹)-O(4)	2.42 (1)
-O(4)	1.47 (1)	O(4)-O(4 ¹)	2.37 (1)
-O(4 ¹)	1.47 (1)	O(4 ¹)-O(1)	2.42 (1)
Average	1.47	O(1)-O(4)	2.37 (1)
		O(1 ¹)-O(4 ¹)	2.37 (1)

Table 4 (cont.)

Cu(1)-square plane	
Cu(1)-O(1)	1.999 (8) Å
Average	1.999
Cu(2)-square plane	
Cu(2)-O(2)	1.902 (12) Å
-O(3)	1.886 (10)
-O(4)	1.980 (8)
-O(4 ¹)	1.980 (8)
Average	1.937
Cu(2)-O(1)	3.069 (8) Å

Table 5. *Valence angles*

B(1)-tetrahedron		
O(1)-B(1)-O(2)	111 (1)°	
O(2)-O(3)	108 (1)	
O(3)-O(4)	111 (1)	
O(4)-O(1)	108 (1)	
O(1)-O(3)	107 (1)	
O(2)-O(4)	108 (1)	

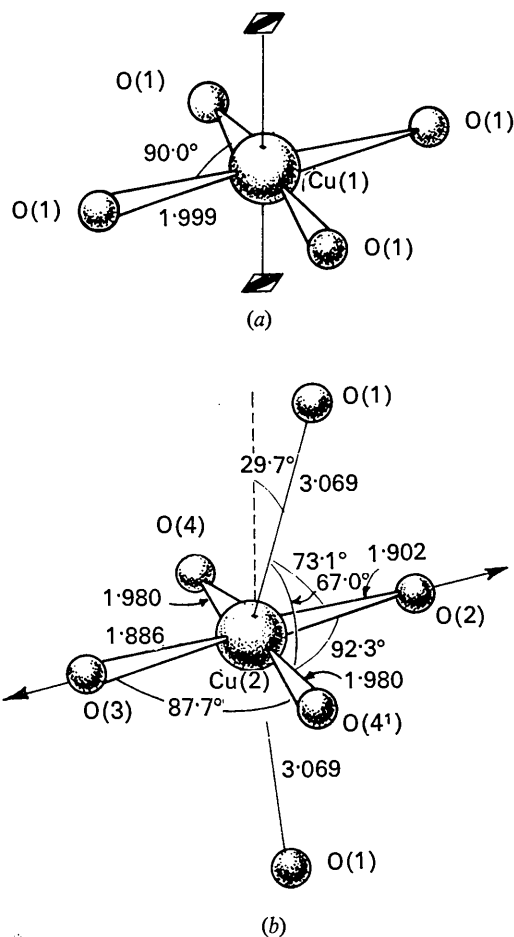


Fig. 4. The oxygen atom arrangement around (a) $\text{Cu}(1)$, (b) $\text{Cu}(2)$. The bond lengths in Å, and corresponding valence angles are given.

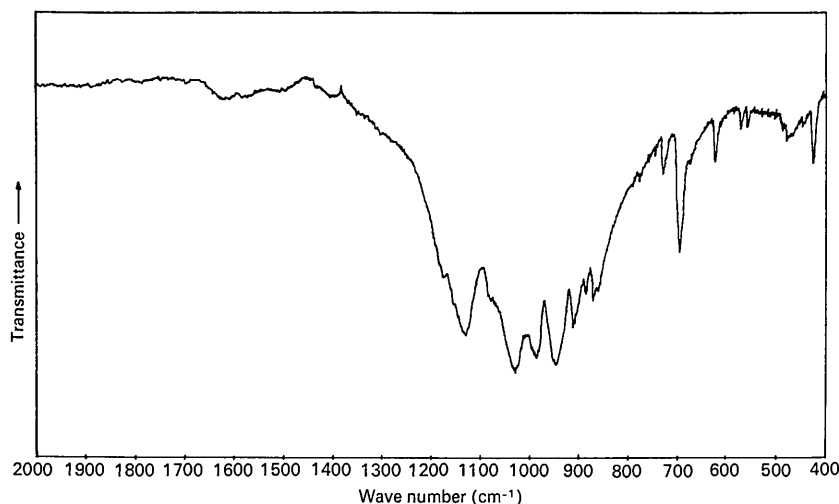


Fig. 5. Infrared spectrum of copper metaborate.

Table 5 (cont.)

B(2)-tetrahedron		
O(1)–B(2)–O(1 ¹)	114	(1)°
O(1 ¹)–O(4)	110	(1)
O(4)–O(4 ¹)	107	(1)
O(4 ¹)–O(1)	110	(1)
O(1)–O(4)	106	(1)
O(1 ¹)–O(4 ¹)	106	(1)
Cu(1)-square plane		
O(1)–Cu(1)–O(1)	90.0	(3)°
Cu(2)-square plane		
O(2)–Cu(2)–O(4)	92.3	(4)°
O(4)–O(3)	87.7	(3)
O(3)–O(4 ¹)	87.7	(3)
O(4 ¹)–O(2)	92.3	(4)
O(1)–Cu(2)–O(2)	73.1	(4)
O(1)–O(4 ¹)	67.0	(2)

The numerical calculations were carried out on the 7070 IBM computer of the Centro de Cálculo Electrónico del C.S.I.C., Spain and on the 7090 IBM computer of the Centro de Cálculo de la Universidad de Madrid, Spain. This work forms part of the Ph. D. Thesis of one of us (M.M.R.) who also acknowledges the research grant given by Ministerio de Educación y Ciencia, Spain.

References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORNL Report TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- DERNIER, P. D. (1969). *Acta Cryst.* B25, 1001.
- HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* 63, 1737.
- MAREZIO, M., PLETTINGER, H. A. & ZACHARIASEN, W. H. (1963a). *Acta Cryst.* 16, 594.
- MAREZIO, M., PLETTINGER, H. A. & ZACHARIASEN, W. H. (1963b). *Acta Cryst.* 16, 390.
- MAREZIO, M. & REMEIK, J. P. (1966). *J. Chem. Phys.* 44, 3348.
- MAREZIO, M., REMEIK, J. P. & DERNIER, P. D. (1969a). *Acta Cryst.* B25, 955.
- MAREZIO, M., REMEIK, J. P. & DERNIER, P. D. (1969b). *Acta Cryst.* B25, 965.
- MIGHELL, A. D., PERLOFF, A. & BLOCK, S. (1966). *Acta Cryst.* 20, 819.
- SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* 12, 600.
- WEIR, C. E. & SCHROEDER, R. A. (1964). *J. Res. Nat. Bur. Stand.* 68A, 465.
- ZACHARIASEN, W. H. (1963). *Acta Cryst.* 16, 385.
- ZACHARIASEN, W. H. (1964). *Acta Cryst.* 17, 749.
- ÅSRINK, S. & NORRBY, L. J. (1970). *Acta Cryst.* B26, 8.