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## Pentadecacopper(II) Bisdiborate Hexaorthoborate Dioxide

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### Abstract

$\text{Cu}_{15}[(\text{B}_2\text{O}_3)_2](\text{BO}_3)_6|\text{O}_2]$  with the oxide formula  $3\text{CuO} \cdot \text{B}_2\text{O}_3$  crystallizes in space group  $P\bar{1}$  with  $a = 3.353$  (2),  $b = 19.665$  (7),  $c = 19.627$  (8) Å,  $\alpha = 88.77$  (3),  $\beta = 69.71$  (2),  $\gamma = 69.24$  (2)°,  $Z = 10$ ,  $D_x = 4.51$ ,  $D_m = 4.4$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 13.95$  mm<sup>-1</sup>;  $R = 0.03$  for 3407 reflections contributing to the refinements.  $3\text{CuO} \cdot \text{B}_2\text{O}_3$  builds up a layer structure. The structure consists of almost planar  $\text{B}_2\text{O}_5$  groups, planar isolated  $\text{BO}_3$  groups, isolated  $\text{O}^{2-}$  ions, and  $\text{Cu}^{2+}$  ions with a fourfold planar coordination. It is the first reported structure with isolated  $\text{B}_2\text{O}_5$  and  $\text{BO}_3$  groups in conjunction with isolated  $\text{O}^{2-}$  ions.

### Introduction

In the binary system  $\text{CuO}-\text{B}_2\text{O}_3$  only two compounds have been reported by Weir & Schroeder (1964), Ecker (1966), Lecuir & Guillermet (1971), Martínez-Ripoll, Martínez-Carrera & García-Blanco (1971), Uhlig (1976), and Richter (1976). These compounds have molar ratios of copper oxide to boron oxide of 1:1 and 3:1. The structure of the metaborate  $\text{CuO} \cdot \text{B}_2\text{O}_3$  has been determined by Martínez-Ripoll *et al.* (1971). Until now only infrared and X-ray powder data of  $3\text{CuO} \cdot \text{B}_2\text{O}_3$  were available. Infrared spectra show, however, that the structure of  $3\text{CuO} \cdot \text{B}_2\text{O}_3$  must be more complex than that of other compounds with formula  $3\text{MO} \cdot \text{B}_2\text{O}_3$  ( $M = \text{Mg}, \text{Mn}, \text{Co}, \text{Ni}$ ) which have been studied in detail.

### Experimental

Single crystals of  $3\text{CuO} \cdot \text{B}_2\text{O}_3$  were grown in a platinum crucible from a nearly stoichiometric melt (3% excess  $\text{B}_2\text{O}_3$ ). Most crystals obtained by this method were in the form of thin plates, frequently intergrown. They all showed perfect cleavage on (100)

and the form {100} was the most prominent. For the X-ray investigations a nearly isometric crystal with natural forms {100}, {011}, {0 $\bar{1}1$ }, and {001} was selected. The dimensions of the pinacoidal crystal could be described by the distances of the faces from crystal centre with: (100) 32, (011) 18, (0 $\bar{1}1$ ) 31, and (001) 22  $\mu\text{m}$ .

The space group and crystal data were determined by equi-inclination Weissenberg and precession photographs, using  $\text{Cu } K\alpha$  radiation. Lattice constants were refined from 16 Bragg reflections, measured on a Picker diffractometer. The lattice parameters were reduced using Delaunay's method. The unreduced cell (the setting of which is closely related to the crystal shape) proved to be more convenient in the following considerations.

Data collection: 8500 reflections,  $3.5^\circ \leq 2\theta \leq 50^\circ$ , Picker four-circle diffractometer, graphite monochromator,  $\text{Mo } K\alpha$  radiation,  $\theta/2\theta$  scan, scan speed  $0.5^\circ \text{ min}^{-1}$ , scan range  $\Delta 2\theta = 2^\circ$  plus dispersion correction, background  $2 \times 40$  s, three standard reflections every 50 reflections with variations  $\leq 3\%$ . Data reduction: XRAY system (1976) on a Univac 1108 computer, Lorentz and polarization corrections (XRAY system, *DATCO5*, *DATRDN*), absorption correction, using the Gaussian quadrature method (XRAY system, *ABSORB*) with  $7 \times 7 \times 7$  sample points and the optically measured crystal dimensions as listed above. After averaging 3939 symmetrically independent reflections, 2724 had  $I(hkl) > 5\sigma(I)$ ;  $\sigma(I)$  from counting statistics.

### Structure determination

Since direct methods failed, Patterson maps were used. They showed the presence of a nearly planar tetragonal layer structure, with the layers having almost tetragonal symmetry. Polarized infrared single-crystal measurements also indicated that B should be coordinated in a planar fashion to three O atoms and that all

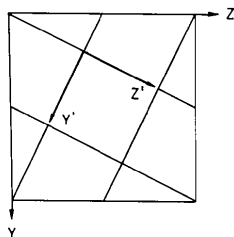


Fig. 1. The relation between small and original unit cells.  $Y = b$  and  $Z = c$  in the original unit cell;  $Y'$  and  $Z'$  are the axes of the chosen subcell.

these  $\text{BO}_3$  triangles should have a planar orientation in the (100) plane.

In  $P\bar{1}$  the positions of 15 independent Cu atoms had to be determined; this should produce 870 maxima in the Patterson map. Because of the nearly tetragonal symmetry in the (100) plane the structure solution with the Patterson function seemed to be impossible by standard procedures. If only the highest peaks of the Patterson map were considered, a two-dimensional nearly quadratic subcell could be chosen containing only one fifth of the projection onto (100) of the original cell. The symmetry of the projection approximates  $p4gm$ . The relation between the small and original unit cells is shown in Fig. 1. Most of the strong reflections can be related to the selection of the subcell. It led to approximate positions for the Cu atoms. After these atomic positions had been transferred into the original large unit cell, 26 nearly correctly positioned

Cu atoms appeared. Their positions could be refined. All other atoms could be found from additional Fourier maps and refinements. Atomic scattering factors for  $\text{Cu}^{2+}$ ,  $\text{O}^-$  and B were taken from Cromer & Mann (1968), and the dispersion correction factors, applied only to the Cu atoms, were taken from *International Tables for X-ray Crystallography* (1974). With isotropic thermal parameters and an isotropic-extinction correction factor the structure was refined to  $R = 0.056$ . Since anisotropic temperature factors of some O and B atoms became negative, refinement of anisotropic temperature factors was carried out for Cu atoms only. It was checked that all atomic positional parameters of the anisotropic refinement ( $R = 0.027$ ,  $R_w = 0.031$ , extinction factor =  $1.378 \times 10^{-3}$ ) differ by less than the e.s.d. from those given here. Because of the large number of parameters the refinement was carried out with Cu-atom parameters and O,B-atom parameters each forming a single block. (Final  $R = 0.03$ ,  $R_w = 0.034$ , extinction factor =  $1.451 \times 10^{-3}$ , parameter-shift/parameter error  $< 0.1$  for each parameter, final average shift/error ratio  $< 0.024$ .)

Table 1 lists the final atomic parameters.\*

\* Lists of structure factors, anisotropic thermal parameters, bond lengths and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36960 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and isotropic thermal parameters ( $\text{\AA}^2 \times 10^2$ ), with e.s.d.'s in parentheses

For Cu:  $U_{\text{eq}} = \sum_i U_{ii}/3$  after diagonalization of the U tensor.

	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$		x	y	z	$U_{\text{iso}}$
Cu(1)	0	0	0	0.9 (1)	O(13)	0.080 (3)	0.1128 (4)	0.3669 (4)	1.4 (2)
Cu(2)	0.0671 (5)	0.03284 (7)	0.17352 (7)	1.0 (1)	O(14)	0.003 (3)	0.1749 (4)	0.4704 (4)	1.1 (2)
Cu(3)	-0.0556 (5)	0.04031 (7)	0.56932 (7)	1.1 (1)	O(15)	0.174 (3)	0.2998 (4)	0.3978 (4)	1.5 (2)
Cu(4)	-0.0190 (5)	0.09290 (7)	0.69999 (7)	1.1 (1)	O(16)	0.005 (3)	0.3092 (4)	0.5269 (4)	0.9 (2)
Cu(5)	0.0912 (5)	0.17187 (7)	0.21122 (7)	1.0 (1)	O(17)	0.212 (3)	0.2504 (4)	0.6320 (4)	1.1 (2)
Cu(6)	0.0642 (5)	0.21743 (7)	0.37772 (7)	1.1 (1)	O(18)	-0.212 (3)	0.1505 (4)	0.8885 (4)	0.9 (2)
Cu(7)	0.0862 (5)	0.20253 (7)	0.55858 (7)	1.1 (1)	O(19)	-0.012 (3)	0.2933 (4)	0.7594 (4)	1.3 (2)
Cu(8)	-0.0992 (5)	0.22389 (7)	0.82850 (7)	1.1 (1)	O(20)	-0.162 (3)	0.2695 (4)	0.9193 (4)	1.3 (2)
Cu(9)	-0.1075 (5)	0.18373 (7)	0.96812 (7)	1.1 (1)	O(21)	0.004 (3)	0.2111 (4)	0.0516 (4)	1.1 (2)
Cu(10)	-0.1308 (5)	0.30911 (7)	0.09916 (7)	1.1 (1)	O(22)	-0.206 (3)	0.3542 (4)	0.0092 (4)	1.2 (2)
Cu(11)	0.0825 (5)	0.38819 (7)	0.35001 (7)	1.0 (1)	O(23)	-0.258 (3)	0.4078 (4)	0.1366 (4)	0.9 (2)
Cu(12)	0.1334 (5)	0.34898 (7)	0.60150 (7)	1.0 (1)	O(24)	-0.041 (3)	0.3582 (4)	0.2679 (4)	1.2 (2)
Cu(13)	0.1346 (5)	0.37585 (7)	0.77133 (7)	1.0 (1)	O(25)	0.001 (3)	0.4764 (4)	0.3075 (4)	1.3 (2)
Cu(14)	-0.1375 (5)	0.44019 (7)	0.04234 (7)	1.0 (1)	O(26)	0.061 (3)	0.4097 (4)	0.4503 (4)	1.3 (2)
Cu(15)	-0.0980 (5)	0.44300 (7)	0.21237 (7)	1.0 (1)	O(27)	0.272 (3)	0.3927 (4)	0.6739 (4)	0.9 (2)
Cu(16)	0	0.5	0.5	0.9 (1)	O(28)	0.043 (3)	0.4530 (4)	0.5860 (4)	0.9 (2)
O(1)	-0.000 (3)	0.0985 (4)	0.0202 (4)	1.0 (2)	O(29)	-0.002 (3)	0.3729 (4)	0.8817 (4)	1.0 (2)
O(2)	0.018 (3)	0.0206 (4)	0.9007 (4)	1.2 (2)	O(30)	0.229 (3)	0.4562 (4)	0.8126 (4)	1.0 (2)
O(3)	-0.042 (3)	0.1267 (4)	0.1420 (4)	1.2 (2)	B(1)	-0.005 (4)	0.1442 (6)	0.0737 (7)	1.0 (2)
O(4)	0.020 (3)	0.5235 (4)	0.0555 (4)	1.1 (2)	B(2)	0.054 (4)	0.2896 (6)	0.2421 (6)	0.9 (2)
O(5)	0.186 (3)	0.0774 (4)	0.2473 (4)	1.0 (2)	B(3)	0.134 (4)	0.0574 (6)	0.3154 (7)	1.0 (2)
O(6)	0.153 (3)	0.0443 (4)	0.4661 (4)	1.2 (2)	B(4)	0.073 (4)	0.1088 (7)	0.4388 (7)	1.0 (2)
O(7)	-0.149 (3)	0.0097 (4)	0.6661 (4)	1.1 (2)	B(5)	0.075 (4)	0.3397 (7)	0.4642 (7)	1.3 (3)
O(8)	0.145 (3)	0.1114 (4)	0.5993 (4)	1.0 (2)	B(6)	0.092 (4)	0.2405 (6)	0.7038 (7)	1.0 (2)
O(9)	0.047 (3)	0.1789 (4)	0.7323 (4)	1.6 (2)	B(7)	-0.104 (4)	0.0800 (6)	0.8624 (7)	0.9 (2)
O(10)	-0.137 (2)	0.0622 (4)	0.7986 (4)	0.8 (2)	B(8)	-0.118 (4)	0.3311 (6)	0.9403 (6)	0.8 (2)
O(11)	0.022 (3)	0.2676 (4)	0.1797 (4)	1.1 (2)	B(9)	0.102 (4)	0.4617 (6)	0.6507 (6)	0.7 (2)
O(12)	0.187 (3)	0.2288 (4)	0.2781 (4)	1.2 (2)	B(10)	0.079 (4)	0.4394 (7)	0.8818 (7)	1.2 (2)

## Description and discussion of the structure

Fig. 2 shows an orthogonal projection of the structure in a polyhedron presentation of the (100) plane. All the atoms build up a pseudotetragonal nearly planar layer structure. The maximum displacement from the *bc* plane is  $<0.45$  (1) Å for the Cu atoms; for all other atoms the maximum is  $<0.85$  (1) Å. The O atoms form nearly two-dimensional close packing, this being a combination of hexagonal closest packing and quadratic packing. All quadratic gaps are occupied by Cu atoms and one third of the trigonal gaps by B atoms. By translation along *a* all layers become equivalent. This translation causes a small lateral displacement of 1.5 Å of the layers relative to each other.

Within each layer the Cu atoms have a nearly quadratic planar coordination to four O atoms. Some of the Cu atoms seem to have additional coordinations to one or two O atoms in the neighbouring layers. From a consideration of the lengths of these additional Cu—O bonds three different types of coordination for the Cu atoms may be distinguished, following Wells's (1975) notation: (i) quadratic planar coordination (4); (ii) distorted tetragonal-pyramidal coordination (4 + 1); (iii) stretched octahedral coordination (4 + 2).

In the *bc* plane all  $\text{CuO}_4$  squares are linked by common O atoms, but in different ways. Certain  $\text{CuO}_4$  squares have common vertices, others have common edges. In this way either blocks of two or linear blocks of four  $\text{CuO}_4$  squares are formed. Within these blocks

remarkably short Cu—Cu distances are found, the shortest being 2.783 (2) Å [the shortest interatomic distance in metallic copper is 2.551 (1) Å]. Even in the linear blocks of four Cu atoms, pairs of Cu atoms are formed.

All B atoms have trigonal-planar coordination to three O atoms within the same layer. Some of the B atoms form isolated  $\text{BO}_3$  groups, others are bridged through a common O atom and form  $\text{B}_2\text{O}_5$  groups. Furthermore, there are isolated  $\text{O}^{2-}$  ions, which are coordinated to three Cu atoms. The O atoms have a nearly regular threefold coordination to Cu or B atoms.

It is evident that the structure is mainly determined by the strong tendency of the Cu atoms, as well as of the B atoms, to retain their typical quadratic-planar or trigonal-planar coordination sphere to O atoms. The close packing in the *bc* plane of the  $\text{CuO}_4$  squares and the  $\text{BO}_3$  triangles leads to strong deviations of their bond distances and angles from the values expected for the free groups. For all  $\text{BO}_3$  and  $\text{B}_2\text{O}_5$  groups the mean B—O distance is calculated as 1.37 (2) Å, which agrees with the values reported by Donnay & Donnay (1973), Coulson & Dingle (1968) and Tennyson (1963) for B—O distances in  $\text{BO}_3$  groups. Nevertheless, individual B—O distances spread over a wide range from 1.32 (2) Å to 1.42 (2) Å, while the O—B—O valence angles show variations from 108.4 (10) to 130.6 (12)°. The B—O—B angles of the two  $\text{B}_2\text{O}_5$  groups are 129.6 (9) and 129.7 (10)° and are comparable with the B—O—B angles of 131.5° found in suanite (Takéuchi, 1952). In spite of the strong deviations in bond lengths and angles the planarity of the individual  $\text{BO}_3$  groups is quite well preserved. The maximum displacement for any B atom out of its  $\text{O}_3$  coordination sphere was less than 0.03 (2) Å.

The Cu—O bonds can be separated into strong Cu—O bonds within the layers and weaker bonds to atoms in the neighbouring layers. The Cu—O bonds of the quadratic coordination in the *bc* plane show large variations in bond lengths and angles: mean Cu—O 1.95 (1) Å, mean O—Cu—O 89.9 (4)°, maximum Cu—O 2.157 (10) Å, minimum Cu—O 1.855 (8) Å, maximum O—Cu—O 106.8 (4)°, minimum O—Cu—O 68.9 (4)°. The shortest Cu—O distances to O atoms in the neighbouring *bc* planes vary from 2.420 (8) to 2.837 (8) Å.

The structure of the other borates with the same oxide formula  $3\text{MO} \cdot \text{B}_2\text{O}_3$  ( $M = \text{Mg}, \text{Mn}, \text{Co}, \text{Ni}$ ) is quite different from that described here. The mineral kotoite,  $3\text{MgO} \cdot \text{B}_2\text{O}_3$ , and the related isotypic compounds (Berger, 1949; Watanabe, 1939) are built up only of isolated  $\text{BO}_3$  groups between which the cations have an almost regular octahedral coordination. Even with all  $\text{BO}_3$  groups having the same orientation these structures cannot be seen as a layer structure, since there is no preference as regards the orientation of the octahedra. To the knowledge of the author  $3\text{CuO} \cdot \text{B}_2\text{O}_3$

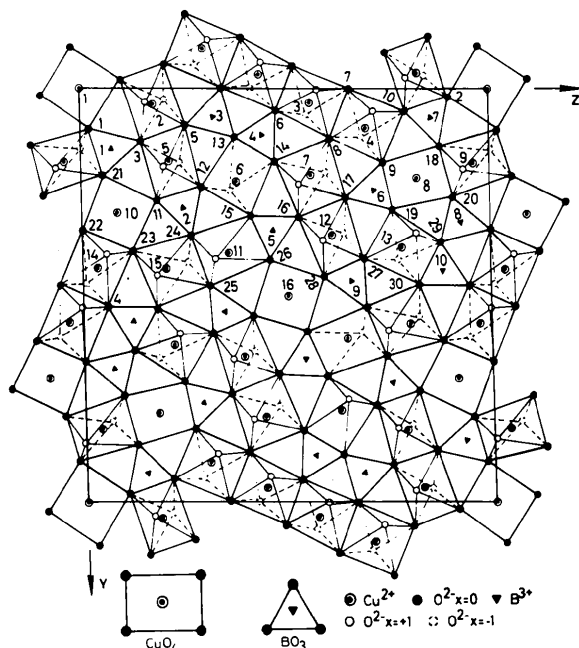


Fig. 2. Orthogonal projection of the structure of  $3\text{CuO} \cdot \text{B}_2\text{O}_3$  on the (100) plane.  $X = 0, \pm 1$  indicates the relative heights of the O atoms with regard to the plane of the drawing.

is the only structure in which the isolated anions  $B_2O_5^{4-}$ ,  $BO_3^{3-}$  and  $O^{2-}$  are found together. The formula of this compound which represents a new type of structure should therefore be written as  $Cu_{15}[(B_2O_5)_2|(BO_3)_6|O_2]$ , with  $Z = 2$ . Since other cations like  $Pd^{2+}$  or  $Cr^{2+}$  show similar behaviour, it can be expected that they will form isotypic or similar borate structures. The palladium metaborate  $PdB_2O_4$ , isotypic with  $CuB_2O_4$ , has just been synthesized by Depmeier (1981).

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## Preparation and Structure of Technetium Triphosphide and Rhenium Triphosphide, Isotypic Polyphosphides with Metal Chains

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#### Abstract

$TcP_3$  and  $ReP_3$  (prepared by reaction of the elemental components in the presence of iodine, and also in a tin flux) crystallize in a new structure type with four formula units in space group  $Pnma$  and the following lattice constants.  $TcP_3$ :  $a = 15.359$  (5),  $b = 3.092$  (1),  $c = 5.142$  (2) Å,  $V = 244.2$  (2) Å<sup>3</sup>;  $ReP_3$ :  $a = 15.354$  (8),  $b = 3.122$  (2),  $c = 5.130$  (2) Å,  $V = 245.9$  (3) Å<sup>3</sup>. The structure was determined from X-ray diffractometer data from a  $TcP_3$  single crystal and refined to a residual value of 0.022 for 996  $F$  values and 15 variables. The metal atoms ( $T$ ) are approximately octahedrally surrounded by P atoms. The P atoms are tetrahedrally coordinated to  $T$  and P atoms with the oxidation numbers  $-2$ ,  $-1$ , and zero. The resulting oxidation number of the metal atoms is  $+3$  ( $d^4$  system). Each metal atom forms two metal–metal bonds across the common edges of adjacent octahedra. Thus all spins are compensated in agree-

ment with the diamagnetism observed for  $ReP_3$ . The structure can be described as a stacking of identical layers of puckered pentagons and hexagons. In this way it is closely related to the structures of many compounds with compositions  $TX_2$  and  $TX_4$  ( $X = P, As, Sb, S, Se$ ).

#### Introduction

During our investigation of the Re–P system we have prepared and characterized the compounds  $ReP_4$  (Jeitschko & Rühl, 1979),  $Re_2P_5$  (Rühl & Jeitschko, 1982), and  $Re_6P_{13}$  (Rühl & Jeitschko, 1980). We had also recognized the existence of another Re polyphosphide of which we did not find crystals large enough for a structure determination. Recently, however, single crystals of the corresponding isotypic phase in the Tc–P system, designated as ‘phase  $D$ ’ (Rühl,