Acta Cryst. (1983). C**39**, 20–22

Hexasodium (*cyclo*-Decahydroxotetracosaoxohexadecaborato)dicuprate(II) Dodecahydrate, $Na_6[Cu_2\{B_{16}O_{24}(OH)_{10}\}].12H_2O$

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(*Received* 4 *May* 1982; *accepted* 4 *August* 1982)

Abstract. $M_r = 1208\cdot2$, triclinic, $P\bar{1}$, $a = 9\cdot171\,(3)$, $b = 10\cdot744\,(4)$, $c = 11\cdot784\,(4)$ Å, $\alpha = 103\cdot08\,(2)$, $\beta = 110\cdot58\,(3)$, $\gamma = 109\cdot53\,(3)°$, $V = 943\cdot49$ Å^3, $Z = 1$, $D_x = 2\cdot13$, $D_m = 2\cdot09$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu(\text{Mo } K\alpha) = 1\cdot336$ mm^{-1}; $R = 0\cdot033$ for 3148 reflections. The structure contains the largest known isolated borate ion, with 16 B atoms. Each borate anion is ring-like and encloses two Cu^{2+} ions, thereby forming a chelate-like complex. This Cu coordination leads to an anomalous proton distribution for the borate anion.

Introduction. The existence of various hydrated Cu borates has been reported by Rosenheim & Leyser (1921), Kesans & Khadorchenko (1957), Kesans (1955), Boiko (1957), and Khundkar & Haider (1956), but only the structure of the mineral bandylite, $Cu[B(OH)_4]Cl$, has so far been determined (Collin, 1951; Fornaseri, 1950, 1951).

Since little is known about the composition of the remaining Cu borates and since the published methods of preparation often lead to results which are not reproducible, a new investigation of the system Na_2O–CuO–B_2O_3–H_2O appeared to be of interest. This is the only system in which a crystalline hydrated Cu borate has so far been synthesized (Rosenheim & Leyser, 1921).

Experimental. Single crystals of $Na_6[Cu_2\{B_{16}O_{24}(OH)_{10}\}].12H_2O$ (Behm, 1982) were obtained by the method described by Rosenheim & Leyser (1921). At the beginning of the crystallization blue-green crystals appeared while the mother liquor became almost colourless. These blue-green crystals seem to be those reported previously. A chemical analysis by these authors led to a composition close to $2Na_2O.3CuO.9B_2O_3.38H_2O$. After a few weeks new dark-blue crystals grew from the same solution. The small yield of the new compound prevented a quantitative chemical analysis. The composition $Na_6[Cu_2\{B_{16}O_{24}(OH)_{10}\}].12H_2O$ was established by X-ray structure analysis. These new dark-blue crystals frequently show pinacoidal habit and seem to be more stable in air at room temperature than those formed first. Nevertheless, decomposition of some of the crystals – probably caused by dehydration – was observed.

X-ray investigations: a crystal with forms $\{001\}$, $\{1\bar{1}0\}$, $\{0\bar{1}1\}$, distances of the faces from crystal centre: (001) 29, $(1\bar{1}0)$ 43, $(0\bar{1}1)$ 108 μm, space group and crystal data from precession photographs, lattice parameters refined from 16 Bragg reflections, measured on a Picker diffractometer, after reducing the cell by Delaunay's method.

Data collection: 6811 reflections, $4° \le 2\theta \le 50\cdot5°$, Picker four-circle diffractometer, graphite monochromator, Mo $K\alpha$ radiation, $\theta/2\theta$ scan, scan speed $1\cdot0°$ min^{-1}, scan range $\Delta 2\theta = 1\cdot75°$ plus dispersion correction, background 2 × 10 s, three standard reflections every 50 reflections.

Data reduction: XRAY system (1976) on a Univac 1108 computer, Lorentz and polarization corrections [XRAY system (1976), *DATCO5*, *DATRDN*], absorption correction, using the Gaussian quadrature method [XRAY system (1976), *ABSORB*] with 5 × 6 × 6 sample points and optically measured crystal dimensions as listed above.

All further calculations made with the program *SHELXTL* (Sheldrick, 1981) on a NOVA-3 computer, averaging gave 3148 symmetrically independent reflections with $|F| \ge 3\sigma_F$, σ_F from counting statistics, merge R value $= 0\cdot0094$, atomic scattering and dispersion-correction factors for Cu, Na, O, B, and H from *International Tables for X-ray Crystallography* (1974).

The structure was solved by Patterson methods. Direct methods with *SHELXTL* led to similar results, but in the early stage of structure determination these results were rejected because of the unexpected concentration of the heavy atoms and their short interatomic distance of only $2\cdot97$ Å. With the two Cu atoms all other non-hydrogen atoms could be found from Fourier maps and refinements. With anisotropic thermal parameters for all these atoms the structure was refined to $R = 0\cdot041$, a goodness of fit value of $1\cdot378$ and a slope value for the normal probability plot of $1\cdot059$. In the following difference Fourier map 17 H atoms could be located from the highest remaining peaks. Refinements including the H atoms without restrictions led to unrealistically short O—H distances, although no H atom coalesced with its neighbouring O

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Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* ($Å^2$) *with e.s.d.'s*

$U_{eq} = \sum_i U_{ii}/3$ after diagonalization of the **U** tensor.

	x	y	z	U_{eq}
Cu	0·53833 (5)	0·48760 (4)	0·38665 (3)	0·0120 (2)
Na(1)	0·8549 (2)	0·0811 (2)	0·8773 (1)	0·0304 (7)
Na(2)	0·8493 (2)	0·0483 (1)	0·3676 (1)	0·0219 (6)
Na(3)	0·5737 (2)	0·2260 (2)	0·8678 (2)	0·0370 (8)
O*w*(1)	0·4640 (3)	0·0107 (3)	0·2523 (3)	0·030 (1)
O*w*(2)	0·7884 (4)	0·4431 (3)	0·6108 (3)	0·048 (2)
O*w*(3)	0·8991 (5)	0·3564 (4)	0·8828 (4)	0·061 (2)
O*w*(4)	0·5803 (3)	0·1567 (3)	0·5257 (3)	0·033 (1)
O*w*(5)	0·7919 (3)	0·2007 (3)	0·0362 (3)	0·032 (1)
O*w*(6)	0·6468 (3)	0·4725 (3)	0·9322 (2)	0·027 (1)
O*e*(1)	0·1572 (3)	0·3449 (3)	0·1580 (2)	0·024 (1)
O*e*(2)	0·8919 (3)	0·2856 (2)	0·3979 (2)	0·025 (1)
O*e*(3)	0·8796 (3)	0·1093 (2)	0·6819 (2)	0·020 (1)
O*e*(4)	0·1641 (3)	0·0185 (2)	0·8372 (2)	0·021 (1)
O*e*(5)	0·3639 (3)	0·1766 (2)	0·6490 (2)	0·021 (1)
O(1)	0·1876 (3)	0·1709 (2)	0·2446 (2)	0·015 (1)
O(2)	0·8674 (3)	0·4871 (2)	0·3596 (2)	0·019 (1)
O(3)	0·1797 (3)	0·1691 (2)	0·4404 (2)	0·014 (1)
O(4)	0·3952 (3)	0·3728 (2)	0·4463 (2)	0·018 (1)
O(5)	0·2923 (3)	0·3765 (2)	0·6435 (2)	0·015 (1)
O(6)	0·0919 (3)	0·3427 (2)	0·7407 (2)	0·016 (1)
O(7)	0·4269 (3)	0·3280 (2)	0·2169 (2)	0·015 (1)
O(8)	0·4231 (3)	0·2082 (2)	0·0110 (2)	0·014 (1)
O(9)	0·1598 (3)	0·1344 (2)	0·0312 (2)	0·019 (1)
O(10)	0·6437 (3)	0·2489 (2)	0·2180 (2)	0·016 (1)
O(11)	0·0764 (3)	0·1415 (2)	0·5943 (2)	0·015 (1)
O(12)	0·6386 (3)	0·4467 (2)	0·1534 (2)	0·013 (1)
B(1)	0·2346 (4)	0·2205 (3)	0·5841 (3)	0·013 (1)
B(2)	0·2235 (4)	0·4471 (4)	0·7215 (3)	0·013 (1)
B(3)	0·5317 (4)	0·3095 (3)	0·1482 (3)	0·012 (1)
B(4)	0·2355 (4)	0·2464 (4)	0·1623 (3)	0·013 (1)
B(5)	0·2569 (4)	0·2411 (3)	0·3785 (3)	0·012 (1)
B(6)	0·2499 (5)	0·1223 (4)	0·9626 (3)	0·015 (1)
B(7)	0·7994 (5)	0·3422 (4)	0·3252 (3)	0·015 (2)
B(8)	0·0209 (4)	0·2001 (4)	0·6735 (3)	0·013 (1)

atom. Therefore, the H-atom positions from the difference Fourier map were accepted. Only their isotropic temperature factors were refined together with all parameters of the other atoms. The refinement results are: $R = 0·0328$ with unit weights, a goodness of fit value of 1·051 and a normal probability slope value of 0·896; $F(000) = 606$. Table 1 lists the final atomic parameters.*

Discussion. Figs. 1 and 2 show the molecular structure of the anion $[Cu_2\{B_{16}O_{24}(OH)_{10}\}]^{6-}$, with bond lengths and angles given in Table 2. The anion is formed by B—O triangles and tetrahedra which share O corners in such a manner that the whole polyborate framework surrounds the two central Cu atoms as in a chelate complex. The Cu atoms have a nearly quadratic planar coordination to four O atoms of the polyborate framework (Fig. 3). Further O atoms have Cu—O distances > 3·0 Å and do not complete an octahedral coordination sphere for the Cu atoms.

In the polyborate ring framework typical six-membered cyclic (B_3O_3) subunits can be distinguished from connecting BO_3 groups. In these (B_3O_3) subunits one B atom has trigonal-planar coordination to O while the other two B atoms are tetrahedrally coordinated. These two B atoms connect the (B_3O_3) subunits to each other or to BO_3 groups. Three (B_3O_3) subunits with neighbouring pairs rotated 90° with respect to each other together with one BO_3 group build up one half of

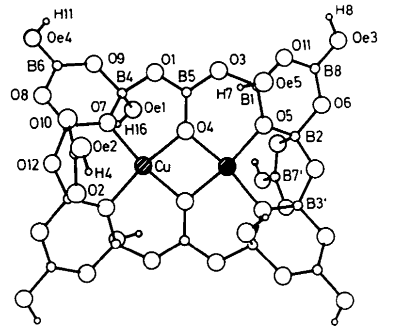

Fig. 1. The complex Cu borate anion with numbering of the atoms.

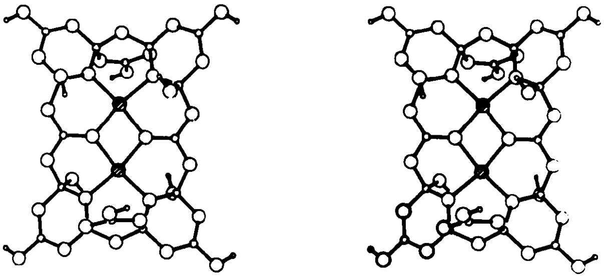

Fig. 2. A stereoscopic view of the complex anion.

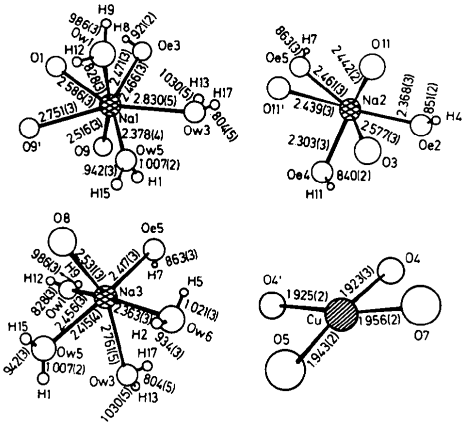

Fig. 3. Coordination spheres of the Cu and Na atoms with distances (Å).

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* Lists of structure factors, H-atom parameters, anisotropic thermal parameters and bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38103 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s*

Cu–O(4)	1·923 (3)	O(4)–Cu–O(7)	91·2 (1)
Cu–O(7)	1·956 (2)	O(4)–Cu–O(4′)	78·9 (1)
Cu–O(4′)	1·925 (2)	O(7)–Cu–O(5)	97·6 (1)
Cu–O(5)	1·943 (2)	O(4′)–Cu–O(5)	92·5 (1)
B(1)–O*e*(5)	1·453 (5)	O(3)–B(1)–O*e*(5)	109·9 (3)
B(1)–O(3)	1·490 (4)	O(5)–B(1)–O*e*(5)	113·5 (2)
B(1)–O(5)	1·482 (4)	O(5)–B(1)–O(3)	112·0 (3)
B(1)–O(11)	1·478 (5)	O(11)–B(1)–O*e*(5)	106·8 (3)
		O(11)–B(1)–O(3)	104·9 (2)
		O(11)–B(1)–O(5)	109·2 (3)
B(2)–O(5)	1·494 (5)	O(6)–B(2)–O(5)	112·0 (3)
B(2)–O(6)	1·472 (5)	O(2)–B(2)–O(5)	106·1 (3)
B(2)–O(2)	1·499 (5)	O(2)–B(2)–O(6)	107·0 (3)
B(2)–O(12)	1·428 (3)	O(12)–B(2)–O(5)	111·2 (3)
		O(12)–B(2)–O(6)	109·4 (3)
		O(12)–B(2)–O(2)	111·0 (3)
B(3)–O(7)	1·489 (5)	O(8)–B(3)–O(7)	112·7 (2)
B(3)–O(8)	1·463 (3)	O(10)–B(3)–O(7)	107·2 (3)
B(3)–O(10)	1·499 (5)	O(10)–B(3)–O(8)	107·3 (3)
B(3)–O(12)	1·445 (4)	O(12)–B(3)–O(7)	109·6 (3)
		O(12)–B(3)–O(8)	109·3 (3)
		O(12)–B(3)–O(10)	110·7 (2)
B(4)–O*e*(1)	1·465 (5)	O(1)–B(4)–O*e*(1)	107·0 (3)
B(4)–O(1)	1·486 (5)	O(7)–B(4)–O*e*(1)	109·6 (2)
B(4)–O(7)	1·478 (4)	O(7)–B(4)–O(1)	112·1 (3)
B(4)–O(9)	1·471 (4)	O(9)–B(4)–O*e*(1)	111·4 (3)
		O(9)–B(4)–O(1)	106·0 (2)
		O(9)–B(4)–O(7)	110·6 (3)
B(5)–O(1)	1·378 (4)	O(3)–B(5)–O(1)	116·4 (2)
B(5)–O(3)	1·372 (5)	O(4)–B(5)–O(1)	122·1 (3)
B(5)–O(4)	1·351 (3)	O(4)–B(5)–O(3)	121·5 (3)
B(6)–O*e*(4)	1·378 (4)	O(8)–B(6)–O*e*(4)	117·1 (4)
B(6)–O(8)	1·358 (4)	O(9)–B(6)–O*e*(4)	119·5 (3)
B(6)–O(9)	1·359 (5)	O(9)–B(6)–O(8)	123·4 (3)
B(7)–O*e*(2)	1·374 (5)	O(2)–B(7)–O*e*(2)	120·0 (2)
B(7)–O(2)	1·366 (4)	O(10)–B(7)–O*e*(2)	117·6 (3)
B(7)–O(10)	1·358 (3)	O(10)–B(7)–O(2)	122·4 (3)
B(8)–O*e*(3)	1·389 (5)	O(11)–B(8)–O(6)	123·0 (3)
B(8)–O(6)	1·350 (4)	O*e*(3)–B(8)–O(6)	118·9 (4)
B(8)–O(11)	1·345 (5)	O*e*(3)–B(8)–O(11)	118·1 (3)

the polyborate ring framework around a pair of Cu atoms, the other half being related to that just described by an inversion centre halfway between this pair. All O atoms not bonded to two B atoms or coordinated to Cu atoms are protonated [labelled O*e*( )].

The total charge of the anionic Cu borate complex $[Cu_2\{B_{16}O_{24}(OH)_{10}\}]$ is calculated to be −6. In the unit cell this complex is surrounded by Na^+ cations and water molecules. The three symmetrically independent Na^+ cations are coordinated to their neighbours in two different ways. Na(1) has an irregular coordination to seven nearest neighbours, while Na(2) and Na(3) have a strongly distorted octahedral coordination (Fig. 3).

It is worth noting that all O atoms which do not belong to the borate ring framework are those of water molecules [labelled O*w*( )]. The water molecules are bonded *via* O—H···O hydrogen bonds of different strengths, the shortest being 2·708 (3) Å for O(12)—O*w*(6).

The structure of the Cu borate described here shows some peculiarities which are not found in other known borate structures. To the knowledge of the author the discrete borate anion with its 16 B atoms is the largest which has so far been reported. The two central Cu^{2+} cations are fully enclosed within the polyborate anion just as metal cations are complexed in typical organic chelates. It should be mentioned that the Cu atoms are already complexed by borate in the aqueous solution of pH 7 from which the crystals were grown. This was shown by Rosenheim & Leyser (1921) with their investigations of the ionic transport in solution and the colour deepening of the solution. It is, however, impossible to decide what kind of complex anion is formed in solution, because two different kinds of Cu borate crystals could be grown from the same solution.

The two O atoms in the complex which are bonded to one B and coordinated to two Cu behave anomalously, because they are not protonated. This contradicts the borate rules of Christ & Clark (1977) which forbid the occurrence of unprotonated B-bonded O in the presence of water molecules.

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