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RESEARCH ARTICLE

Synthesis and Single Crystal X-ray Structure of the Monoclinic Sodium Copper Borate ($Na_2Cu_2B_{12}O_{21}$)

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Abstract: Sodium copper borate, $Na_2Cu_2B_{12}O_{21}$, is a member of the $Na_2M_2B_{12}O_{21}$ (M(II) = Ni, Cu and Co) structure type. It has been synthesized by a solid-state reaction. Single-crystal XRD analysis showed that it crystallizes in the monoclinic system, I 2/a space-group with a = 17.353(1), b = 4.671(1), c = 19.672(1)Å, ß= 101.42(1)°, Z = 4. The new anhydrous borate shows a 3-D framework crystal structure. It contains a discernible tunnel structure constructed from BO_4 tetrahedra, BO_3 trigonal units and CuO_6 octahedra. Seven-coordinate Na^+ cations lie in the large tunnels that extend along the b axis. This structural model is validated by the charge distribution (CD) analysis.

Keywords: $Na_2Cu_2B_{12}O_{21}$, Crystal structure, X-ray diffraction, Charge distribution

Introduction

Nowadays borates have received great attention of material scientists because they show a great variety of physical properties ranging from nonlinear optical (NLO)[1–4], ferroelectric, piezoelectric[5], to other useful properties for technical applications[6-8]. Some transition metal borates exhibit catalytic activity[9], magnetic behavior[10-12] and reversible Li-ion uptake[13-15]. In addition, a boron atom may adopt triangular oxygen coordination, where three oxygen atoms form B(sp2)–O bonds, or tetrahedral oxygen coordination, where four oxygen atoms form B(sp3)–O bonds. The borate compounds present a rich structural chemistry: the BO_3 and BO_4 groups may be further linked via common oxygen atoms to form isolated rings and cages or polymerize into infinite chains, sheets and networks, leading to a great structural complexity[16,17].

The present work deals with preparation and crystal structures of the new monoclinic sodium copper borate $Na_2Cu_2B_{12}O_{21}$ possessing an isotypic with two structures of $Na_2Co_2B_{12}O_{21}$[13] and $Na_2Ni_2B_{12}O_{21}$[18].

Experimental

Numerous starting materials were employed for the solid-state synthesis, including $Na_2HAsO_4.7H_2O$, $(NH_4)_2HPO_4$, $Cu(acac)_2.H_2O$, CuO, $Ba(NO_3)_2$ and H_3BO_3. Materials in the molar ratio of Na:P:Cu:Ba:B = 6:2:9:2:34 were ground to a fine powder in an agate mortar.

The mixture was gradually heated to 1100 K. After the mixture melted completely, it was cooled down to 900 K at a rate of 2 °C/h, followed by cooling to room temperature at 30 °C/h. The title crystals could be obtained from the top section of the solidified melt. Besides, the semi-quantitative energy-dispersive spectroscopy (EDS) analysis of one of the blue crystals obtained as mentioned above was performed with a JEOL-JSM 5400 scanning electron microscope; it revealed the presence of Cu, Na and O elements. The formula of the title compound, $Na_2Cu_2B_{12}O_{21}$, has been established as a result of crystal structure.

Results and Discussion

Structure solution and refinement

A single crystal with dimensions 0.37×0.32×0.11 mm^3 was chosen for the structure determination and refinement. The data were collected on an Enraf-Nonius CAD-4 diffractometer using the MoKa radiation at room temperature[19]. The unit-cell parameters were refined using 25 reflections with $10.22 \leq \theta \leq 14.98°$. The intensity data were corrected for Lorentz, polarization and absorption using empirical Ψ-scan correction[20]. The systematic absences in the reduced data uniquely indicated the space group I2/a no. 15[21]. The crystal structure of $Na_2Cu_2B_{12}O_{21}$ was solved by direct methods using SHELXL-97[22] computer program included in the WingX software package[23]. The metal and borate atoms were first located and then all the oxygen atoms were found by successive Fourier difference synthesis. The final cycle of refinement leads to the final discrepancy factors R = 0.0296 and R_W = 0.0832.

The CD computations and structural figures have been obtained with the CHARDI-IT[24] and Diamond 2.0[25] programs, respectively. The crystallographic data and some details of the structure refinement are summarized in Table 1. The final atomic coordinates and the displacement parameters are reported in Tables 2; selected interatomic-distances and angles are given in Table 3. Bond valence computation (V) and charge distribution analysis (Q) are given in Table 4.

Table 1. Crystal data, data collection and refinement

Crystal data	
Chemical formula	$Na_2Cu_2B_{12}O_{21}$
Formula Weight	638.78
Colour / Shape	Blue / Prism
Crystal system	Monoclinic
Space group	*I*2/*a*
Cell dimensions	*a* = 17.3526 (1) Å; *b* = 4.6708 (1) Å; *c* = 19.6724 (10) Å; β = 101.418 (1)°
Cell volume	1562.9 (4) Å^3
Z	4
data collection	
Diffractometer	Enraf-Nonius CAD-4
Temperature	293 K
Radiation, graphite monochromator :	Mo Kα (λ=0.71073 Å)
scan mode	w – 2θ
Theta range for data collection	2.1 – 27.0°

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Range of h, k, l	$-22 \leq h \leq 22$, $-5 \leq k \leq 1$, $-25 \leq l \leq 25$
Measured reflections	1694
Independent reflections	1386 [R_{int}= 0.027]
Refinement	
Refinement method	Full-matrix least-squares on F^2
Parameters	169
$S(F^{2)}$	1.05
Final R indices [$I > 2\sigma(I)$]	R_1= 0.023; wR= 0.063
$(\Delta\rho)_{max}$ / $(\Delta\rho)_{min}$	0.42/−0.36 (e.Å^{-3})

Table 2. Atomic coordinates and U_{eq} temperature factors for $Na_2Cu_2B_{12}O_{21}$.U_{eq} = 4/3 Σi Σj $a_i a_j$ U_{ij}

Atom	x	y	z	U_{eq}(Å^2)
Cu	0.941667 (14)	1.00914 (6)	0.547874 (13)	0.00959 (11)
Na	0.84979 (6)	1.0892 (2)	0.36014 (6)	0.0234 (2)
B1	0.93447 (13)	1.5493 (5)	0.44276 (12)	0.0073 (5)
B2	0.62801 (14)	1.2406 (6)	0.33523 (12)	0.0104 (5)
B3	0.93102 (14)	0.9066 (6)	0.24711 (13)	0.0104 (5)
B4	0.49137 (14)	1.4342 (6)	0.33843 (12)	0.0086 (5)
B5	0.68775 (14)	1.5843 (5)	0.51536 (13)	0.0081 (5)
B6	0.71017 (14)	0.8789 (6)	0.41341 (12)	0.0106 (5)
O1	0.96485 (9)	1.4061 (3)	0.39308 (8)	0.0095 (3)
O2	0.87650 (9)	1.4118 (3)	0.46938 (8)	0.0097 (3)
O3	0.95935 (8)	0.8166 (4)	0.46360 (7)	0.0106 (3)
O4	0.69126 (9)	1.0655 (4)	0.35737 (8)	0.0145 (4)
O5	0.86820 (9)	1.0918 (4)	0.22122 (8)	0.0129 (3)
O6	0.56490 (8)	1.2486 (3)	0.36870 (7)	0.0096 (3)
O7	0.92821 (8)	0.7633 (3)	0.30648 (8)	0.0113 (3)
O8	0.51193 (9)	1.6395 (3)	0.29014 (7)	0.0104 (3)
O9	0.65538 (8)	0.7913 (4)	0.45146 (7)	0.0103 (3)
O10	0.78486 (8)	0.7809 (4)	0.42537 (8)	0.0113 (3)
O11	3/4	1.4153 (5)	1/2	0.0085 (4)

Table 3. Main interatomic distances (Å) and bond angles (°) for $Na_2Cu_2B_{12}O_{21}$

CuO_6 Octahedron				
Cu-	O3^{i}	1.954 (1)	O3^{i}—Cu—O3	78.78 (7)
	O3	1.963 (1)	O3^{i}—Cu—O9^{ii}	171.22 (6)
	O9^{ii}	1.970 (1)	O3—Cu—O9^{ii}	92.62 (6)
	O6^{ii}	2.008 (1)	O3^{i}—Cu—O6^{ii}	93.20 (6)
	O2	2.551 (1)	O3—Cu—O6^{ii}	171.59 (6)
	O1^{i}	2.646 (1)	O9^{ii}—Cu—O6^{ii}	95.47 (6)
			O1^{i}—Cu— O3^{i}	83.07 (6)
			O1^{i} —Cu—O6^{ii}	100.30 (6)
			O1^{i} —Cu—O3	81.37 (6)
			O1^{i} —Cu—O9^{ii}	93.97 (6)
			O2—Cu—O1^{i}	165.00 (6)

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			O2 —Cu—O9^{ii}	96.19 (6)
			O2 —Cu—O3	87.17 (6)
			O2 —Cu—O6^{ii}	89.70 (6)
			O2—Cu—O3^{i}	83.07 (6)
B(1)O$_3$ trigonal unit				
B1-	O3^{iii}	1.358 (3)	O3^{iii}—B1—O1	121.3 (2)
	O1	1.373 (3)	O3^{iii}—B1—O2	121.7 (2)
	O2	1.381 (3)	O1—B1—O2	117.0 (2)
B(2)O$_3$ trigonal unit				
B2-	O4	1.369 (3)	O4—B2—O5^{iv}	115.8 (2)
	O5^{iv}	1.371 (3)	O4—B2—O6	121.6 (2)
	O6	1.385 (3)	O5^{iv}—B2—O6	122.6 (2)
B(3)O$_3$ trigonal unit				
B3-	O7	1.355 (3)	O7—B3—O8^{iv}	122.7 (2)
	O8^{iv}	1.360 (3)	O7—B3—O5	117.3 (2)
	O5	1.406 (3)	O8^{iv}—B3—O5	119.8 (2)
B(4)O$_4$ tetrahedron				
B4-	O8	1.443 (3)	O8—B4—O1^{v}	107.5 (1)
	O1^{v}	1.456 (3)	O8—B4—O7^{vi}	113.3 (1)
	O7^{vi}	1.475 (3)	O1^{v}—B4—O7^{vi}	108.6 (1)
	O6	1.560 (3)	O8—B4—O6	109.3 (1)
			O1^{v}—B4—O6	110.9 (1)
			O7^{vi}—B4—O6	107.3 (1)
B(5)O$_4$ tetrahedron				
B5-	O11	1.418 (3)	O11—B5—O2^{ii}	112.5 (1)
	O2^{ii}	1.454 (3)	O11—B5—O10^{vii}	111.9 (1)
	O10^{vii}	1.486 (3)	O2^{ii}—B5—O10^{vii}	108.6 (1)
	O9^{iii}	1.597 (3)	O11—B5—O9^{iii}	109.5 (1)
			O2^{ii}—B5—O9^{iii}	109.5 (1)
			O10^{vii}—B5—O9^{iii}	104.6 (1)
B(6)O$_3$ trigonal unit				
B6-	O10	1.351 (3)	O10—B6—O9	123.0 (2)
	O9	1.383 (3)	O10—B6—O4	114.7 (1)
	O4	1.393 (3)	O9—B6—O4	122.3 (2)
	Na-	O10	2.359 (1)	
		O7	2.419 (1)	
		O1	2.467 (1)	
		O2	2.590 (1)	
		O4	2.743 (1)	
		O3	2.801 (1)	
		O5	2.814 (1)	

Symmetry codes: (i) −x+2, −y+2, −z+1; (ii) −x+3/2, y, −z+1; (iii) x, y+1, z; (iv) −x+3/2, −y+5/2, −z+1/2; (v) x−1/2, −y+3, z; (vi) x−1/2, −y+2, z; (vii) −x+3/2, y+1, −z+1; (viii) x+1/2, −y+3, z; (ix) x, y−1, z; (x) x+1/2, −y+2, z; (xi) −x+3/2, y−1, −z+1

Table 4. Bond valence computation (V) and charge distribution analysis (Q) for $Na_2Cu_2B_{12}O_{21}$

Atom	B1	B2	B3	B4	B5	B6	Cu	Na	O1	O2
V	3.01	2.98	2.99	2.96	2.95	2.98	1.98	0.90	-2.04	-2.00
Q	2.93	3.06	3.04	3.02	3.00	2.99	1.99	0.98	-2.02	-1.98

Atom	O3	O4	O5	O6	O7	O8	O9	O10	O11
V	-2.03	-2.04	-1.97	-1.98	-1.98	-1.86	-1.96	-2.02	-1.79
Q	-2.14	-2.04	-1.93	-1.92	-2.05	-1.94	-1.88	-2.11	-1.99

Further details of the crystal structure may be obtained from the Fachin formation szentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD–422498 .

Bond valence (BV) and charge distribution (CD) analysis

The charge distribution CD method[24,26–29] is the most recent development of the classical theory of bond strength[30] and differs from the bond valence (BV) approach[31,32] in exploiting the experimental bond distances rather than employing empirical curves. Both bond valence model and charge distribution analysis show that the structure is well refined with satisfactory valences (V) / charges (Q) for all atoms (Table 4).

Crystal structure description and discussion

The new anhydrous borate shows a 3-D framework crystal structure. It contains a discernible tunnel structure constructed from CuO_6 octahedra, BO_4 tetrahedra and BO_3 trigonal units (Figure 1).

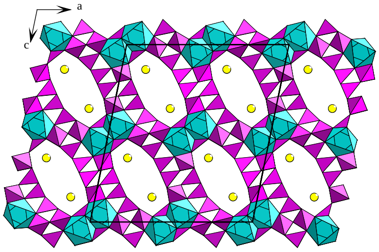

Figure 1. Polyhedral representation of the tri-dimensional framework $Na_2Cu_2B_{12}O_{21}$ structure viewed along the b-axis showing the tunnels along the [010] direction

The borate framework may also be described as a full condensation of the 12-oxygen rings illustrated in Figure 1. The centrosymetric 24-membered ring is composed of eight BO_3 triangles and four BO_4 tetrahedra. The linkage is made by sharing oxygen vertices (Figure 2). The cross-sectional dimensions of the tunnel are 4.46 Å x 8.45 Å (atom to atom). Boron atoms of each $B_{12}O_{24}$ ring are lying nearly planar parallel to approximately (2-12) or (212).

Figure 3 illustrates that each borate ring is connected to six equivalent adjacent rings by sharing oxygen vertex. The angle between two adjacent rings being 101.2°. When the connectivity of this spacious structure is extended, we see that the tunnel is bounded by symmetry-related pairs of BO_3^{3-}, $B_3O_7^{5-}$ and $B_4O_9^{6-}$ units (Figure 2). The borate units are stacked along the b-axis forming a 3D-dimensional network with void spaces (cavities, pockets) filled by Cu^{2+} and open channels occupied by Na^+ cations. These cations stabilize the void regions within the anion structure by adopting charge compensating and space filling roles.

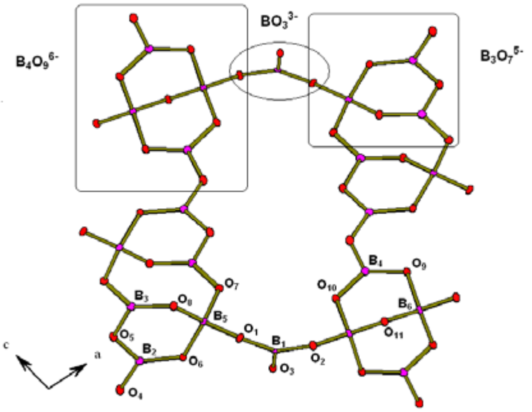

Figure 2. Representation of the ($B_{11}O_{22}$) borate group existing in $Na_2Cu_2B_{12}O_{21}$. It consists of the association of B_3O_7, B_4O_{10} and BO_3 borate groups. The linkage is made by O1, O2, O4 and O7 oxygen atoms

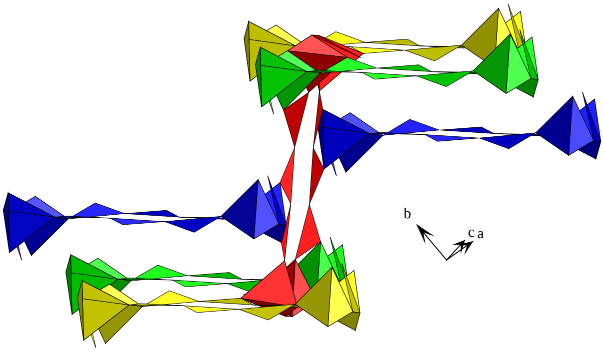

Figure 3. Connection between the borate rings. Each one is connected to six equivalent rings in the $Na_2Cu_2B_{12}O_{21}$ framework

Four $B_{12}O_{24}$ rings fused through the oxygen atoms are responsible of the generation of the void spaces (cavities, pockets) filled by Cu^{2+} cations. Each Cu atom occupies a distorted octahedron (four Cu—O lengths between 1.954 and 2.008 Å, two at 2.551 and 2.646 Å). The stereochemistry of the divalent copper (d^9) ion causes [4 + 2] octahedral distortion according to the Jahn-Teller effect. Two of these octahedra share an edge to form a bioctahedral dimer $Cu_2O_{10}^{4+}$ (Figure 1). Each dimer interleave between successive borate units equivalent by b translation. Thus, these dimers are separated and isolated along the *b*-axis by intervening borate groups.

Seven-coordinate Na^+ cations lie in the large tunnels that extend along the b axis. Relatively high values of thermal displacements of these atoms indicate that these loosely bound ions perform thermally activated movements within the framework tunnels.

The average values for the B—O distances are 1.371 (3) Å, 1.375 (3) Å, 1.374 (3) Å, 1.484 (3) Å, 1.489 (3) Å and 1.376 (3) Å, respectively for $B(1)O_3$, $B(2)O_3$, $B(3)O_3$, $B(4)O_4$, $B(5)O_4$ and $B(6)O_3$ groups. The Na-O distances range from 2.359 (1) Å to 2.814 (1) Å for NaO_7 polyhedra. These geometrical characteristics are very similar to those observed in the related oxide compounds so far known[33-37].

Conclusion

The structure of the $Na_2Cu_2B_{12}O_{21}$ new compound consists of BO_n (n= 3, 4) polyhedra and CuO_6 octahedra sharing corners and edges to form a tree-dimensional framework. Na^+ cations are located in the large tunnels. CuO_6 exhibits strong elongation due to [4 + 2] Jahn-Teller effect (Cu–O: 2.551 and 2.646 Å), whereas BO_n octahedron are regular. Both bond valence model and charge distribution analysis show that the structure is well refined.

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