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Unprecedented Formation of Potassium Borate Based Carbonate from Chloral Hydrate, Potassium Carbonate and Boric Acid

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The structure of the reaction product of boric acid, chloral hydrate, and potassium carbonate in H_2O, potassium bis(carbonato)borate hydrate $K[B(CO_2\text{-}\mu\text{-}O\text{-}CO_2)_2]\cdot 2H_2O$, was determined by X-ray crystallography. The compound crystallized in the orthorhombic system, and was characterized to be in the space group *Aba*2, with cell parameters of $a = 11.0579(10)$Å, $b = 11.1695(10)$Å, $c = 9.0504(9)$Å, $Z = 4$, and $V = 1117.83(18)$Å^3. In the crystal structure, intermolecular O–H···O hydrogen bonds link the molecules into a supramolecular structure, in which they may be effective in stabilizing the structure. The B atom espouses a distorted tetrahedral geometry with four O atoms of carbonate ligands.

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Since B atoms can interact with the O atoms by either sp^2 or sp^3 hybridization to form triangular $[BO_3]^{3-}$ and tetrahedral $[BO_4]^{5-}$ units, attention has been particularly paid to borates due to finding a number uses for material design. B–O groups through polymerization can result in constructing one-dimensional (1D) chains, 2D layers, and 3D networks.[1-4] The wide range of applications of borates virtually stems from the structure-property relationship that renders possible their huge structural varieties and the functionality of the BO units.[5] Such structure diversities make the structure chemistry of borates intriguing. Hitherto, a series of borate materials have been reported for many utilisations, including, birefringence, piezoelectric, pyroelectric, and nonlinear optics.[6-9] Boron compounds formed by a non-metallic support unit can be displayed in a binary fashion comprising of an anionic borate structural unit and a cationic interstitial complex.[10] The role of non-metal cations differs from metal cations, since they generally do not coordinate to oxygen in the same way, and may act instead as hydrogen-bond donors to the structural unit. The inorganic borates, known up to the present, form a broad class of chemical compounds. A dual coordination mode of the boron atom exhibits its unique position of borates among other classes of inorganic compounds including silicates, phosphates, nitrates and carbonates. From this aspect, borates fairly bear a resemblance to organic compounds. Inorganic synthesis of novel borates aimed to design advanced material is of great significance and the reaction conditions for most borates is carried out hydrothermally. In addition to that borates synthesized at elevated temperatures and pressure composed of mainly tetrahedral coordination of most boron atoms are a noteworthy feature, which associate these borates to silicates. Only recently, the structural chemistry of inorganic crystals has been considerably supported by the co-incorporation of more anion units such as $[BO_3]^{3-}$, $[BO_4]^{5-}$, $[CO_3]^{2-}$, $[PO_4]^{3-}$, $[NO_3]^-$, and $[SiO_4]^{4-}$ *etc.*, which culminates in various kinds of multiple-anions compounds, like borate carbonate, borate phosphate, phosphate nitrate, and phosphate silicate *etc.*[11]

Boric acid forms complexes with organic molecules conveying adjacent hydroxyl groups through esterification reactions. While partial esterification creates monoesters (1:1 complex) retaining the planar configuration with no charge or a tetrahedral configuration with negative charge, complete esterification proceeds to the formation of a bicyclic diester (1:2 complex) structures with negatively charged tetrahedral borate anions.[12,13] The cations role in stabilizing the ester structures has been evidenced. Monoesters of boron are reported to be quite labile, and rapidly hydrolyze to their original components in aqueous solution, in the meantime diesters are thermodynamically more stable and almost undissociable in water.[14,15] Bis-chelate complexes of boron containing aromatic or aliphatic diols and carboxylic acids are generally non-toxic, inexpensive thermally and electrochemically stable. From a close look at the literature, the reaction of boron complexes with such ligands is largely in favor of 1:2 complexes, rather than 1:1 complexes. Inspired by

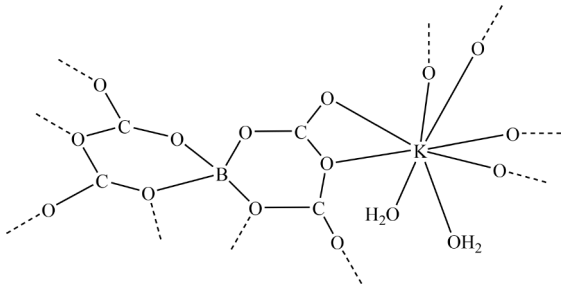

Fig. 1 Chemical diagram of the title compound.

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Table 1 Crystal data and structure refinement parameters for complex **1**

Chemical formula: $C_4H_4BKO_{12}$	
Formula weight = 293.98	
T = 296 K	
Crystal system: orthorhombic	Space group: *Aba2*
a = 11.0579(10)Å	$\alpha = 90^\circ$
b = 11.1695(10)Å	$\beta = 90^\circ$
c = 9.0504(9)Å	$\gamma = 90^\circ$
V = 1117.83(18)Å^3	
Radiation: Mo $K\alpha$	(λ = 071073 Å)
μ(Mo $K\alpha$) = 0.54 mm^{-1}	F(0 0 0) = 592
Crystal size = 0.05 × 0.04 × 0.03 mm^3	
No. of reflections collected = 18910	
No. of independent reflections = 1402	
θ range for data collection = 3.4 to 28.363°	
Data/Restraints/Parameters = 1402/5/91	
Goodness-of-fit on F^2 = 1.06	
R indices [$I > 2\sigma(I)$]: $R1$ = 0.041	
R indices (all data): $R1$ = 0.058, $wR2$ = 0.169	
$(\Delta/\rho)_{max}$ 0.001	
$(\Delta\rho)_{max}$ = 0.64 eÅ^{-3}	$(\Delta\rho)_{min}$= –0.59 eÅ^{-3}
Measurement: D8-QUEST diffractometer	
Programs system: SHELXS-97	
Structure determination: WINGX, MERCURY	
CCDC deposition number: 2072746	

the enormous crystal diversity of boron structures and relying our experience in this field,[16-19] we have pitched upon a diol containing compound, chloral hydrate, and reacted with boric acid at a moderate temperature while hoping that the reaction is completed and forms an anionic diester; lastly, potassium carbonate is added to ensure the cationic charge balance. Herein, breaking off the CO_3^{2-} group from the boric acid-chloral hydrate system in an attempt to obtain bis-chelate complexes supported by K atom were targeted; however, docking of the carbonate group through oxygen sharing surprisingly occurs. A novel inorganic borate compound, K[B(CO_2-μ-O-CO_2)$_2$]·2H_2O, was successfully achieved.

The abovementioned compound (Fig. 1) was prepared by mixing boric acid (10 mmol; 0.618 g) and chloral hydrate (20 mmol; 3.31 g) in an aqueous solution (25 mL). The reaction mixture was allowed to be stirred at 50°C for 1 h, resulting in the formation of a colorless material. To this solution, solid potassium carbonate (5 mmol; 0.694 g) was added with the immediate gas evaluation. The solution was stirred further at 50°C for 3 h. Crystals of the title compound were obtained by slow evaporation.

A suitable crystal of **1** was selected for data collection, which was performed on a D8-QUEST diffractometer equipped with graphite-monochromatic Mo-$K\alpha$ radiation. The structure was solved by direct methods using SHELXS-97[20] and refined by full-matrix least-squares methods on F^2 using SHELXL-97[20] from within the WINGX[21] suite of software. The water H atoms were located in a difference map refined freely. Molecular diagrams were created using MERCURY.[22] Details of data collection and crystal structure determinations are given in Table 1. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 2072746. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). The crystal data and selected bond lengths are summarized in Table 1 and 2, respectively.

Table 2 Selected bond distances for complex **1** (Å)

B1–O2	1.469(7)	B1–O3	1.478(7)
K1–O1	2.820(4)	K1–O5	2.857(4)
K1–O6	2.903(5)	K1–O2^{iii}	3.035(5)

Symmetry code: (iii) x+1/2, –y+1, z+1/2.

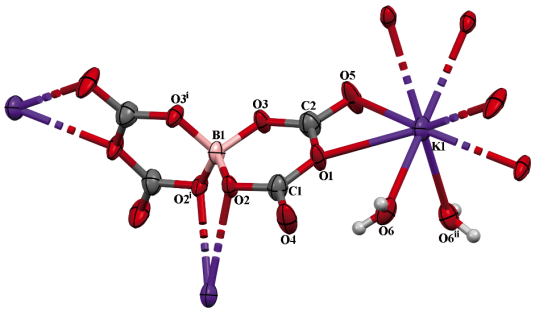

Fig. 2 Molecular structure of **1** showing the atom numbering scheme. [(i) 1–x, 1–y, z; (ii) 2–x, 1–y, z].

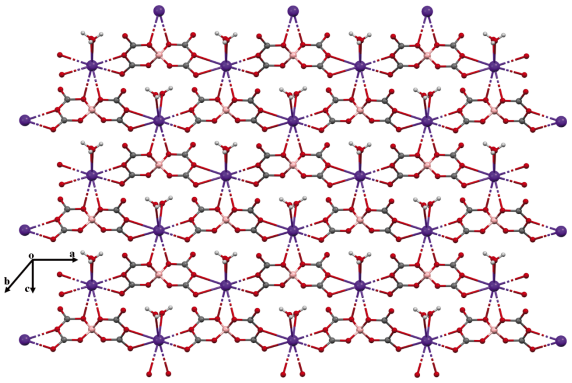

Fig. 3 Infinite 2D supramolecular network in **1**.

An ORTEP perspective view of the compound is displayed in Fig. 2. The X-ray single-crystal study shows that complex **1** has a 2D coordination polymer. The molecular structure of **1**, with the atom numbering scheme, is shown in Fig. 2. The asymmetric unit of complex **1** contains one K(I) ion, half of the fused carbonate molecule and one coordinated aqua ligand. The B1 atom is located on a crystallographic C_2 axis, and is coordinated by four oxygen atoms [B1-O2 = 1.469(7)Å and B1-O3 = 1.478(7)Å]. The K1 atom is also located on the C_2 axis and coordinated by six oxygen atoms [K1-O1 = 2.820(4)Å, K1-O2^{iii} = 3.035(5)Å and K1-O5 = 2.857(4)Å] from fused carbonate molecules and two oxygen atoms [K1-O6 = 2.903(5)Å] from aqua ligands [(iii) x+1/2, –y+1, z+1/2]. The K(I) ions and coupled carbonate molecules are a 2D coordination polymer running parallel to the *ac* plane (Fig. 3). Adjacent to these, 2D coordination polymers are further joined by O–H···O hydrogen bonds (Table 3), generating a 3D supramolecular network (Fig. 4). The K–O and B–O bond distances are fairly similar to those observed in mixed borate and carbonate complexes ($K_9[B_4O_5(OH)_4]_3(CO_3)X{\cdot}7H_2O$ (X = OH and I).[23] The role of unreacted chloral hydrate in this structure would seem to be

Table 3 Hydrogen bond parameters (Å, °)

D-H···A	D H	H···A	D···A	D-H···A
O6-H6A···O2^{vi}	0.83 (3)	2.11 (3)	2.921 (6)	167
O6-H6B···O4	0.83 (3)	1.97 (8)	2.676 (7)	142

Symmetry code: (vi) *x*+1/2, –*y*+1/2, *z*.

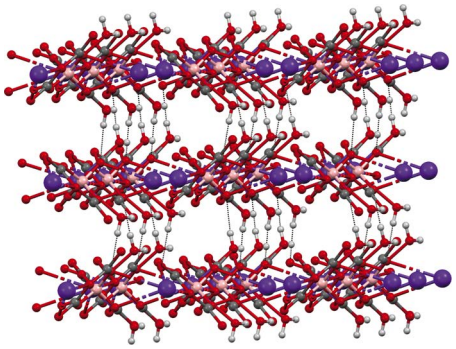

Fig 4 Infinite 3D network in **1**.

incontrovertible, because the reaction between solely using two components (*i.e.* potassium carbonate and boric acid) has been previously reported to produce a tetraborate anion whose formula is $K_2[B_4O_5(OH)_4]\cdot H_2O$.[24] By synthesizing this compound with potassium metal, we have clearly demonstrated that the reaction is reproducible and not a single serendipitous occurrence. It was reported earlier that there are three tools for introducing carbonate ions into the system: the direct addition of carbonate or bicarbonate, atmospheric fixation of carbon dioxide, and *in situ* decomposition of ligands.[25] Within the bounds of these possibilities, the last alternative would appear to be the most conceivable. Nevertheless, the reaction mechanism for this extraordinary structure remains a mystery and needs further clarification, we currently focus on a theoretical base for this particular reaction and akin experimental works are underway to elucidate how this might occur.

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References

1. P. C. Burns, J. D. Grice, and F. C. Hawthorne, *Can. Mineral.*, **1995**, *33*, 1131.
2. A. P. Topnikova and E. L. Belokoneva, *Russ. Chem. Rev.*, **2019**, *88*, 204.
3. H. Huppertz and B. von der Eltz, *J. Am. Chem. Soc.*, , **2002**, *124*, 9376.
4. X. Zhang, H. Wu, H. Yu, Z. Yang, and S. Pan, *SciChinaMater*, **2019**, *62*, 1023.
5. H. P. Wu, H. W. Yu, S. L. Pan, Z. J. Huang, Z. H. Yang, X. Su, and K. R. Poeppelmeier, *Angew. Chem. Int. Ed.*, **2013**, *52*, 3406.
6. K. M. Ok, E. O. Chi, and P. S. Halasyamani, *Chem. Soc Rev.*, **2006**, *35*, 710.
7. R. K. Li and Y. Ma, *CrystEngComm*, **2012**, *14*, 5421.
8. V. P. Solntsev, E. G. Tsvetkov, V. A. Gets, and V. D. Antsygin, *J. Cryst. Growth*, **2002**, *236*, 290.
9. M. Luo, Y. Song, F. Liang, N. Ye, and Z. Linc, *Inorg. Chem. Front.*, **2018**, *5*, 916.
10. N. Hadjadj, M. A. E. Dems, H. Meraziga, and L. Bendjeddoua, *Acta Crystallogr., Sect. C*, **2018**, *74*, 411.
11. C. Huang, F. Zhang, S. Cheng, Z. Yang, H. Li, and S. Pan, *Chem.—Eur. J.*, **2020**, *26*, 16628.
12. M. Bishop, S. G. Bott, and A. R. Barron, *Dalton Trans.*, **2000**, 3100.
13. A. F. Amaral, M. M. Margues, J. A. L. da Silva, and J. J. R. F. da Silva, *New J. Chem.*, **2008**, *32*, 2043.
14. C. D. Hunt, *J. Trace Elem. Exp. Med.*, **2003**, *16*, 291.
15. S. Chapelle and J. F. Verchere, *Tetrahedron*, **1988**, *44*, 4469.
16. R. J. Errington, M. Tombul, G. L. P. Walker, W. Clegg, S. L. Heath, and L. Horsburgh, *J. Chem. Soc.—Dalton Trans.*, **1999**, 3533.
17. M. Tombul, R. J. Errington, R. A. Coxall, and W. Clegg, *Acta Crystallogr., Sect. C*, **2003**, *59*, 231.
18. M. Tombul, K. Güven, O. Büyükgüngör, H. Aktaş, and T. N. Durlu, *Acta Crystallogr., Sect. C*, **2007**, *63*, 430.
19. M. Tombul, K. Güven, and T. N. Durlu, *J. Chem. Cryst.*, **2009**, *39*, 445.
20. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, **2008**, *64*, 112.
21. L. J. Farrugia, *J. Appl. Cryst.*, **1999**, *32*, 837.
22. Mercury, Ver. 3.0; CCDC, available online *via* ccdc.cam.ac.uk/products/mercury.
23. L. Liu, Y. Yang, J. Huang, X. Dong, Z. Yang, and S. Pan, *Chem.—Eur. J.*, **2017**, *23*, 10451.
24. M. K. Dhatchaiyini, M. NizamMohideen, G. Rajasekara, and A. Bhaskarana, *IUCrData*, **2019**, *4*, x190128.
25. A. S. R. Chesman, D. R. Turner, B. Moubaraki, K. S. Murray, G. B. Deacon, and S. R. Batten, *Dalton Trans.*, **2012**, *41*, 10903.