On the nature of tincalconite

RUDY L. LUCK* AND GE WANG

Department of Chemistry, Michigan Technological University, Houghton, Michigan 49931, U.S.A.

ABSTRACT

An examination of synthetic crystalline material by single crystal X-ray diffractometry reveals a unit-cell dimension that was previously ascribed to tincalconite. However, the best fit to the reflection data obtained at 291(2) K is obtained with composition $Na_6[B_4O_5(OH)_4]_3 \cdot 8H_2O$. This formula is different from the $Na_2[B_4O_5(OH)_4] \cdot 3H_2O$ previously assigned to tincalconite from an earlier crystallographic study. Additionally, our model fits best with non-crystallographic measurements and agrees with the analysis from a more recent low temperature crystallographic analysis. Tincalconite is best formulated as $Na_6[B_4O_5(OH)_4]_3 \cdot 8H_2O$. It is trigonal, $R32$, $a = 11.1402$ (11), $c = 21.207$ (3) Å, $Z = 3$, $R = 0.020$ for 512 $F_o > 4\sigma$ (F_o) and 0.021 for all 529 data at 291(2) K.

INTRODUCTION

Giacovazzo et al. (1973) reported a formula of $Na_2[B_4O_5(OH)_4] \cdot 3H_2O$ for tincalconite. The assignment was supported by complementary studies (Christ and Clark 1957; Christ and Garrels 1959; Petch et al. 1962; Cuthbert and Petch 1963a, 1963b) and in fact, the assignment corrected a crystal structure reported by Invers (1948). More recently, there was another crystallographic study at 108(2) K, which established that tincalconite was best formulated as $Na_2[B_4O_5(OH)_4] \cdot 2.667H_2O$ (Powell et al. 1991). However, this composition has not been widely accepted by the scientific community (Attinà et al. 1992; Burns 1995; Kocakuşak et al. 1996; Anovitz and Grew 1996; Anovitz and Hemingway 1996; and Touboul et al. 1999).

We obtained crystals of tincalconite in a reaction designed to probe the existence of extended H-to-H atom intermolecular interactions. This consisted of reacting sodium borohydride in water and tetraheptylammonium iodide in acetone. Unfortunately, the borohydride anion, under these conditions, decomposed (presumably forming the borate anion) and, from this mixture, a crystalline material identified as tincalconite was obtained. We report here a room-temperature single-crystal determination, which agrees with the latest formulation (Powell et al. 1991) and also displays an interesting feature regarding the nature of the disorder that led to the incorrect formulation of Giacovazzo et al. (1973).

EXPERIMENTAL METHODS

Crystals were grown in a glass tube containing $NaBH_4$ in H_2O on the bottom layered with a solution of $[(CH_3(C_6H_{12})]_4 \cdot NI$ in acetone on the top. A suitable crystal was chosen and trimmed using a sharp scalpel. This crystal was rolled in epoxy resin, fixed on top of a glass fiber, and then placed on the diffractometer.

The data collection and reduction were accomplished using the procedures described in Luck and Mendenhall (2000). The windows program WinGX was used as the interface for the solution and refinement of the models (Farrugia 1999). The data were first reduced and corrected for absorption using psi-scans (North et al. 1968) and a model derived using the program SIR97 (Altomare et al. 1999). The structure was refined with SHELXL97 (Sheldrick 1997). The refinement was not straightforward. One of the O atoms (O12) on a general position was described with very large thermal parameters after initial refinement. The refinement was repeated with 50% occupancy of O12 (which would result in the $Na_2[B_4O_5(OH)_4] \cdot 3H_2O$ formulation) but the thermal parameters were still unacceptably large. It was only at occupancies of one-third that this atom refined with acceptable thermal parameters. The H atoms on the borate entity and non-disordered O atom ascribed to a water molecule were located in difference maps and were included in the refinement. The H atoms associated with the disordered O atom were located in difference maps but were refined in fixed positions riding on the disordered O atom site with thermal parameters constrained to be 1.5 times the isotropic equivalent of the O12 atom. The final model, which refined to convergence, consisted of all non-H atoms described with anisotropic thermal parameters. This produced the final figures of merit listed in Table 1. A listing of positional parameters and selected angles and distances are presented in Tables 2 and 3, respectively.

As a final check refinements were done with full, one-half, and one-third occupancy of O12. In addition to producing the most reasonable thermal parameters for O12 the lowest figures of merit were obtained when atom O12 was described at one-third occupancy. It should be noted that a free refinement of the occupancy of O12, with all other atoms included and refined as described above, resulted in a value of 0.337(5), in contrast to the 0.334(5) obtained previously by Powell et al. (1991).

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* Present address: Department of Chemistry, Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931, U.S.A. E-mail: rluck@mtu.edu

TABLE 1. Crystal data and structure refinement details for tincalconite

Formula	$H_{28}B_{12}Na_6O_{27}$
M_r	727.87776
habit	white prism
crystal system	trigonal
space group	$R32$
a (Å)	11.1402(11)
c (Å)	21.207(3)
V (Å³)	2279.3(4)
λ (Mo$K\alpha$ radiation)	0.71073
temperature (K)	291(2)
Z	3
D_x (g/cm³)	1.871
$F(000)$	1301.7
monochromator	graphite
diffractometer	Enraf-Nonius CAD-4
diffraction geometry	κ–geometry diffractometer
type of scan	θ scans
μ (Mo$K\alpha$)(mm⁻¹)	0.254
cryst size/mm	$0.40 \times 0.40 \times 0.20$
cell dimens refinement	
number of reflections	25
2θ range/deg	20–30
semiempirical abs cor*	
no of ψ-scans	333
no. of reflcns	9
transm coeff	
min	0.913
max	0.956
θ max/°	24.95
h	$0 \rightarrow 11$
k	$0 \rightarrow 11$
l	$-25 \rightarrow 25$
no. of reflcns measured	1052
no. of obsd data, III > 2σ(I)	512
no. of parameters	105
R_{int}	0.013
$R(F)$†	0.020
$wR(F^2)$‡	0.059§
Goodness-of-fit	1.116
Max. (Δ/σ)	0.000
Residual $\Delta Q/e$Å⁻³	
max	0.152
min	−0.195

* North et al. 1968.
† $R = \Sigma(F_o - F_c)/\Sigma(F_o)$.
‡ $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.
§ $w = 1 / [s^2(F_o^2) + (0.0402 \times P)^2 + 1.0673P]$, where P = (Max($F_o^2$, 0) + 2 × F_c^2) / 3.

TABLE 2. Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for tincalconite

	x	y	z	U_{eq}
Na1	0	0	0	19(1)
Na2	−3305(1)	0	0	26(1)
Na3	−6667	−3333	740(1)	44(1)
B1	2666(2)	925(2)	1184(1)	16(1)
B2	−5143(3)	919(3)	1207(1)	25(1)
O1	−6667	2002(2)	1667	13(1)
O2	−5029(2)	1222(2)	1836(1)	22(1)
O3	−6249(1)	749(2)	855(1)	23(1)
O4	1952(1)	1294(1)	721(1)	17(1)
O5	−4168(2)	718(2)	915(1)	48(1)
O11	−1991(2)	2443(2)	−322(1)	35(1)
O12	−6279(9)	−4492(8)	1705(7)	66(4)
H121	−6174	−4433	2089	99
H122	−6403	−4940	1375	99
H4	1490(30)	1480(30)	938(12)	31(7)
H5	−3540(40)	880(40)	1111(17)	59(10)
H111	−1540(40)	2770(40)	71(18)	69(11)
H112	−1370(50)	2550(40)	−472(16)	67(12)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. Hydrogen coordinates are listed with their isotropic displacement parameters (Å² × 10³).

DISCUSSION

The structure of tincalconite consists of Na cations and the borate anion held together by a variety of electrostatic interactions. These mostly involve the lone pairs of water molecules, the O atoms in the hydroxyl groups, the Na cations, and some hydrogen bonding interactions.

The nature of the stabilization around each Na cation is unique. The atom Na1, located at the intersection of one three-fold and three twofold axes (Fig. 1), is entirely surrounded by the lone pairs from the O4 atom of the borate anion, resulting in a distorted octahedral geometry (assessed on the basis of closeness to 90°, see relevant angles in Table 2). The atom labeled as Na2, located on a twofold axis (Fig. 2), is surrounded by lone pairs from two O4 atoms, two O5 atoms (also from the borate anion), and two water molecules. The Na2 atom therefore forms a bridge between borate anions. The internal angles around Na2 are descriptive of a more perfect octahedral geometry (see Table 2). The Na3 atom, located on a threefold axis (Fig. 3), is entirely surrounded by lone pairs from what appears to be five water molecules and it is here that we believe that the previous structural work (Giacovazzo et al. 1973) is in error. Three of the sites for the water molecules are fully occupied (labeled as O11_5, H111_5 and H112_5 in Figure 3) and the other two are generated by symmetry. The O11-Na3-O11' angles are very large at 106.56(7)° and the corresponding O11-Na3-O12 and O12-Na3-O12 angles are 75.5(2)° and 66.9(4)° respectively. Atom O12 is on a general position but was refined at one-third occupancy. Therefore, there are two such molecules arranged in a disordered manner in the unit cell resulting in the sixfold pattern displayed in Figure 3. In this diagram only two of the atoms labeled as O12 are involved in each Na3 to Na3' interaction in the unit cell (not the 6 dis-
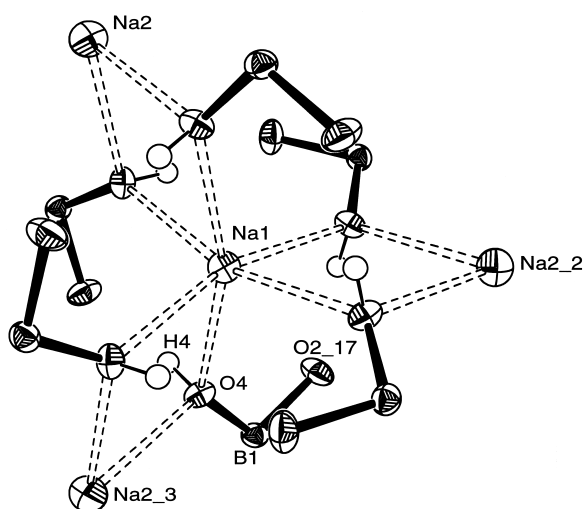
FIGURE 1. An ORTEP-3 for Windows (Farrugia 1997) representation of the bonding environment around Na1. H-atoms are represented by circles of arbitrary radii and ellipsoids are drawn at the 50% probability level. The atom labels that contain a "_" are symmetry generated.

TABLE 3. Selected distances (Å) and angles (°) for tincalconite including Na interactions and some non-bonded interactions

Distances			Angles	
	This work	(108K)*		
Na1-O4	2.4521(13)	2.434(1)	O4-Na1-O4†	85.18(4)
Na1-Na2	3.6813(12)	3.663(1)	O4-Na1-O4‡	163.40(7)
Na2-O11 2.4554(18)	2.436(2)		O4†-Na1-O4‡	85.00(6)
Na2-O5#	2.4687(17)	2.440(3)	O4†-Na1-O4§	107.27(7)
Na2-O5	2.4687(17)		Na2‖-Na1-Na2	120.000(1)
Na2-O4†	2.5008(16)	2.493(2)	O11-Na2-O11#	175.22(10)
Na3-O11#	2.3433(19)	2.335(2)	O11-Na2-O5#	94.23(7)
Na3-O12‡‡	2.441(12)	2.419(8)	O11-Na2-O5	88.41(7)
Na3-O12	2.569(12)	2.544(8)	O5#-Na2-O5	113.08(9)
Na3-Na3§§	3.930(4)	3.902(4)	O11-Na2-O4†	83.98(5)
Na3-H122	2.3730		O5#-Na2-O4†	164.79(6)
B1-O4	1.445(2)	1.442(4)	O5-Na2-O4†	82.02(5)
B1-O1†††	1.466(2)	1.461(3)	O11-Na2-O4‡	92.43(6)
B1-O3†††	1.492(2)		O4†-Na2-O4‡	82.97(7)
B1-O2‡‡‡	1.493(3)		Na1-Na2-Na3	117.83(2)
B2-O5	1.364(3)	1.367(5)	Na3-Na2-Na3#	124.35(3)
B2-O2	1.366(3)	1.361(3)	O11**-Na3-O11††	106.56(7)
B2-O3	1.370(3)	1.374(4)	O11**-Na3-O12‡‡	139.5(3)
O1-B1§§§	1.466(2)		O11††-Na3-O12‡‡	75.5(2)
O2-B1§§§	1.493(3)	1.495(4)	O11#-Na3-O12‡‡	111.5(2)
O3-B1‖‖‖‖‖‖	1.492(2)	1.496(3)	O12‡‡-Na3-O12§§	66.9(4)
O4-H4	0.79(3)		O11**-Na3-O12##	96.0(2)
O5-H5	0.75(4)		O11††-Na3-O12##	148.6(3)
O11-H(111)	0.95(4)		O11#-Na3-O12##	86.93(19)
O11-H(112)	0.72(4)		O12‡‡-Na3-O12##	73.2(3)
O12-O12‡‡	0.765(17)		O12‖‖‖‖-Na3-O12##	53.1(4)
O12-H(121)	0.8200		O12##-Na3-O12***	63.1(4)
O12-H(122)	0.8301		O11**-Na3-Na3§§	112.25(6)
			O4-B1-O1†††	111.58(16)
			O4-B1-O3†††	108.52(14)
			O1†††-B1-O3†††	108.75(14)
			O4-B1-O2‡‡‡	111.14(15)
			O1†††-B1-O2‡‡‡	108.95(14)
			O3†††-B1-O2‡‡‡	107.80(16)
			O5-B2-O2	120.09(19)
			O5-B2-O3	117.67(17)
			O2-B2-O3	122.2(2)
			B1§§§-O1-B1‖‖‖‖‖‖	111.3(2)
			B2-O2-B1§§§	120.84(15)
			B2-O3-B1‖‖‖‖‖‖	117.29(14)
			B1-O4-Na1	135.12(12)
			B1-O4-Na2‖	119.92(11)
			Na1-O4-Na2‖	96.01(5)
			B1-O4-H4	101.7(19)
			Na1-O4-H4	90.7(19)
			B2-O5-Na2	151.89(14)
			B2-O5-H5	115(3)
			Na3#-O11-Na2	114.95(7)
			H(111)-O11-H(112)	92(3)
			Na3§§-O12-Na3	103.3(2)
			H(121)-O12-H(122)	149.2

* Powell et al. 1991.
Symmetry transformations:
† −y,x−y,z.
‡ −x,−x + y,−z.
§ y,x,−z.
‖ −x + y,−x,z.
x−y,−y,−z.
** y−1,x,−z.
†† −x−1,−x + y−1,−z.

‡‡ −x−4/3,−x + y−2/3,−z + 1/3.
§§ x−y−1/3,−y−2/3,−z + 1/3.
‖‖‖‖ y−1/3,x + 1/3,−z + 1/3.
−y−1,x−y,z.
*** −x + y−1,−x−1,z.
††† x + 1,y,z.
‡‡‡ −x−1/3,−x + y−2/3,−z + 1/3.
§§§ −x−1/3,−x + y + 1/3,−z + 1/3.
‖‖‖‖‖‖ x−1,y,z.

played in Fig. 3). Thus, each Na3 atom is pseudo penta-coordinated and only bridged by 2 O atoms (from two solvated water molecules). This shows that tincalconite is best formulated as $Na_6[B_4O_5(OH)_4]_3 \cdot 8H_2O$.

In our opinion, this arrangement may best be described as two $[Na(OH_2)_4]^+$ entities held in close proximity. First, the O11-Na3-O11' angles of 106.6(7)° are very close to the 102.8° observed with isolated $[Na(OH_2)_4]^+$ (Carina et al. 1998). Secondly,

the Na3-O11 distance of 2.433(19) Å is the shortest Na-O atom interaction observed in this structure. This would occur if the Na^+ atom was in need of greater electron density as in $[Na(OH_2)_4]^+$. Third, the Na3-Na3' separation at 3.930(4) Å is much larger than that observed in structures containing two water molecules between two Na atoms: 3.434 Å (Habermann et al. 1992), 3.523 Å (Zheng et al. 1994), 3.527 Å (You et al. 1993), 3.558 Å (Hauptmann et al. 1999), 3.565 (Brechin et al.
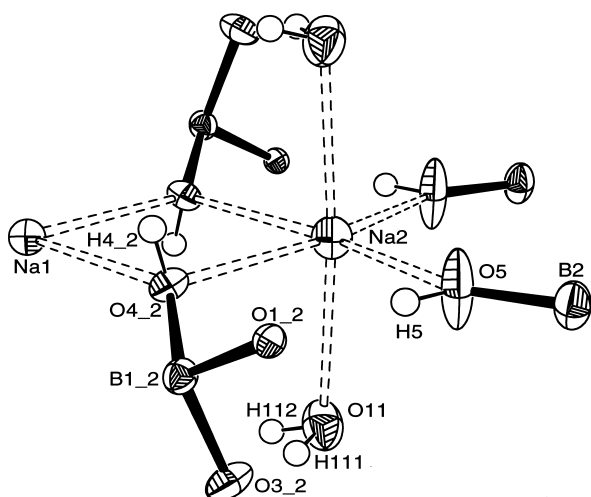
FIGURE 2. An ORTEP-3 for Windows (Farrugia 1997) representation of the bonding environment around Na2. H-atoms are represented by circles of arbitrary radii and ellipsoids are drawn at the 50% probability level. The atom labels that contain a "_" are symmetry generated.
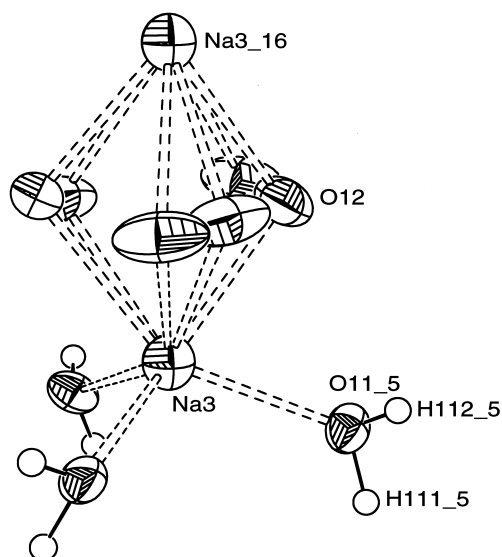

FIGURE 3. An ORTEP-3 for Windows (Farrugia 1997) representation of the bonding environment around Na3. H-atoms are represented by circles of arbitrary radii and ellipsoids are drawn at the 50% probability level. The atom labels that contain a "_" are symmetry generated.

1998), 3.617 Å (Liu et al. 1993), 3.633 Å (Hernandez-Padilla et al. 1992), 3.639 Å (Sileo et al. 1999), and 3.764 Å (Achour et al. 1998). Finally, an asymmetry in the distance of the Na atoms to these "bridging" water molecules was observed in the structure of tincalconite determined both in this study and at lower temperatures (see Table 2). These points provide reasonable evidence that the arrangement is best described as two tetrahedral [Na(OH$_2$)$_4$]$^+$ molecules in close proximity to each other.

The borate anion is depicted in Figure 4, and the relevant bond distances and angles are listed in Table 2. These are not significantly different from those obtained in the previous study

(Giacovazzo et al. 1973) but they are more accurate and agree with those reported more recently (Levy and Lisensky 1978; Janda et al. 1981; Weakley 1985; Powell et al. 1991). The bridging borate O atom (i.e., atoms O1 and O2) of one borate anion is hydrogen bonded to the H atom on the hydroxyl group of an adjacent borate anion (i.e., H4 and H5 respectively) and the other bridging borate O atom (i.e., atom O3) is hydrogen bonded to the H atoms of the ordered solvent water molecule (i.e., H111 and H112; see Table 4). It is through this linkage that the lone pairs on the atom labeled as O11 are suitably located to interact with atom Na3, perhaps resulting in the tetrahedral geometry around Na3. Figure 5 depicts a packing diagram in the unit cell that results from these interactions. This shows that the structure consists of layers of borate anions separated by the solvated Na cations.

On the basis of this study, several conclusions can be made:

(1) The reason for the large thermal parameters for the equivalent atom in the previous determination (Giacovazzo et al. 1973) is now apparent. This atom was clearly disordered as was previously stated by Powell et al. (1991).

(2) Our model also explains why the Na3-Na3' (symmetry generated) distance is 3.930(4) Å and not closer to the 3.30 Å (Frevel 1940; Miller 1936; Grund and Preisinger 1950) and 3.15 Å (Corazza et al. 1967) reported for two Na cations bridged by three water molecules and even longer than the distances for two Na cations bridged by two water molecules as stated above.

(3) The calculated density for our model at 1.87 agrees very well with the measured specific gravity of 1.88 g/cm^3 (Pabst and Sawyer 1948) and for that matter the calculated density of 1.894 g/cm^3 at 108 K (Powell et al. 1991). This is in contrast to the density of 1.94 if tincalconite is formulated as Na$_2$
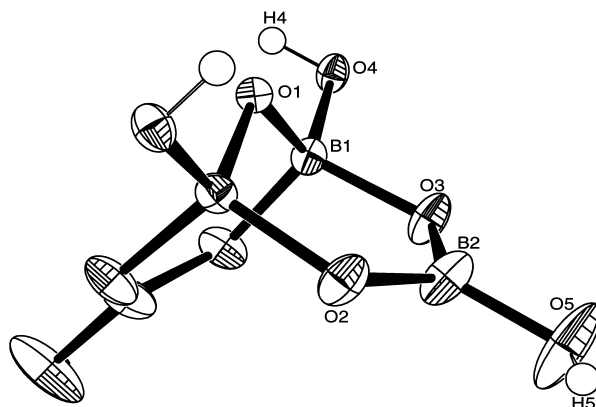

FIGURE 4. An ORTEP-3 for Windows (Farrugia 1997) representation of the borate anion. H-atoms are represented by circles of arbitrary radii and ellipsoids are drawn at the 50% probability level.

TABLE 4. Hydrogen bond listing (Å)

O–H···O	O–H	H···O	O···O	O–H···O
O4–H4···O2*	0.79(3)	2.04(3)	2.833(3)	176(3)
O5–H5···O1†	0.75(5)	1.93(5)	2.680(3)	176(4)
O11–H111···O3‡	0.95(4)	1.84(4)	2.769(2)	168(5)
O11–H112···O3*	0.72(6)	2.21(6)	2.876(3)	155(6)

Symmetry operations:
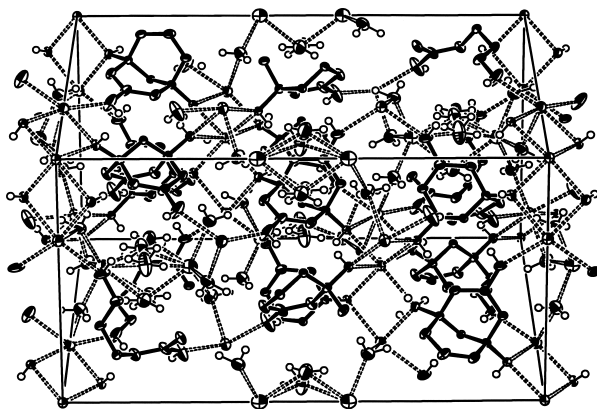* −y,x−y,z.
† −x + y,−x,z.
‡ y,x,−z.

FIGURE 5. A packing diagram showing the unit-cell arrangement found for tincalconite using the program ORTEP-3 for Windows (Farrugia 1997).

$[B_4O_5(OH)_4)]\cdot 3H_2O$.

(4) For $Na_6[B_4O_5(OH)_4)]_3\cdot 8H_2O$ the H_2O content is 29.5 wt%. This is closer to the value of 30.0 wt% for the mineral tincalconite (Pabst and Sawyer 1948) than is $Na_2[B_4O_5(OH)_4)]\cdot 3H_2O$ at 30.9 wt%.

(5) Tincalconite can be obtained by a variety of synthetic strategies with the difference being that the material in this report was obtained at room temperature.

(6) The major difference between the structure at 108(2) K and 291(2) K appears to be the shrinkage in the electrostatic interaction between the various Na cations and the surrounding O atoms. This is most easily observed in shortening of the Na3-Na3' distances as listed in Table 2.

(7) Tincalconite is best formulated as $Na_6[B_4O_5(OH)_4)]_3\cdot 8H_2O$.

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