

Crystal Structures of Sodium Sulfate Decahydrate (Glauber's Salt) and Sodium Tetraborate Decahydrate (Borax). Redetermination by Neutron Diffraction*

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Single-crystal neutron-diffraction data with full-matrix least-squares refinements have yielded precise locations for all atoms (for the H atoms in particular), in both compounds. Hydrogen bonding with H atom sites disordered with equal occupancy, as previously postulated to be the source of zero-point entropy in the sulfate, is quantitatively verified. A thermally excited librational mode of the sulfate ion involving a rearrangement of hydrogen bonding has been found. The two structures, which have closely similar chains of Na ions with coordinated water molecules, are compared in detail. Measures of disagreement are: for the sulfate, $R(F^2) = 0.082$ for $1750 F^2 > \sigma(F^2)$; for the borate, $R(F^2) = 0.060$ for $1837 F^2 > \sigma(F^2)$.

Introduction

The possible utility of certain crystalline hydrate salts as working media for thermal energy storage has stimulated a renewed interest in an understanding of their properties. Reported here are results of a reexamination, by single-crystal neutron diffraction, of the structures of sodium sulfate decahydrate (Glauber's salt) and of sodium tetraborate decahydrate (borax). Both were previously studied by X-ray diffraction, the former by Ruben, Templeton, Rosenstein & Olovsson (1961) and the latter by Morimoto (1956). The present work, in addition to confirming fully the conclusions of both earlier studies, provides accurate locations for the H atoms, improved precision for the remaining atoms, and a full description of the thermal displacements. In the case of the sulfate, an alternative arrangement of hydrogen bonds associated with the excitation of a librational mode of the sulfate ion has been discovered. A detailed comparison is made of the sodium-water chains existing in the two salts, the close similarity of which seems to be the basis for the utility of borax as a nucleating agent for the crystallization of Glauber's salt from aqueous solution (Telkes, 1952). The hypothesis of Ruben *et al.* (1961) concerning disorder of H atoms in the sulfate structure, which accounts for the residual entropy, is confirmed.

Experimental

Specimens of both compounds were grown from aqueous solutions by slow evaporation, and crystal

quality was checked by X-ray precession photography. Cell parameters were determined by least-squares refinement from the first moments of neutron diffractometer 2θ scans recorded at 23.5 °C using a wavelength of 1.0155 Å, based on $a(\text{NaCl}) = 5.6403$ Å. This value was determined by X-ray diffraction using Cu $K\alpha$ radiation, $\lambda = 1.54051$ Å, on the same specimen used to establish the neutron wavelength.

Crystal data

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$: $P2_1/c$, $Z = 4$, $a = 11.512$ (3), $b = 10.370$ (3), $c = 12.847$ (2) Å, $\beta = 107.789$ (10)°.
 $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8\text{H}_2\text{O}$: $C2/c$, $Z = 4$, $a = 11.885$ (1), $b = 10.654$ (1), $c = 12.206$ (1) Å, $\beta = 106.623$ (5)°.

Intensity measurements were made with neutrons monochromatized by reflection at $2\theta = 52.5^\circ$ from (110) planes of a beryllium single crystal. Both specimens were enclosed in thin-walled vitreous silica cylinders. The beam divergence was about 1°; the wavelength was 1.0155 Å with a spread of about 1% full width at half maximum. Reflections were integrated in 2θ scans having 42 to 62 steps at intervals of 0.05° 2θ , with background measured at both ends. A preliminary absolute scale was obtained by comparison with reflections from a standard NaCl specimen. For the sulfate, a 44.3 mg specimen yielded 2789 non-extinguished data for $2\theta \leq 75^\circ$ of which 2636 were symmetry-unique. Intensities of all $h00$ reflections with h odd were vanishingly small; the same evidence of pseudosymmetry was noted in the X-ray intensities by Ruben *et al.* (1961). For the borate, a 16.05 mg specimen yielded 2502 non-extinguished data for $2\theta \leq 95^\circ$ of which 2373 were symmetry-unique; in addition, a sample of 139 extinguished reflections (hkl with $h + k$ odd or $h0l$ with l odd) were scanned to confirm the space-group assignment. Absorption corrections were

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made by means of a 512-point Gaussian quadrature (Busing & Levy, 1957) (program *DATALIB*)* with linear absorption coefficients 0.0238 mm^{-1} for the sulfate and 0.06975 mm^{-1} for the borate.

H atoms were located by means of Fourier syntheses with phases based on the X-ray structures with H atoms omitted; terms were omitted for which $|F_o F_c| < \frac{1}{2} N f_H^2 \ln P$ with $N = 80$ (the number of omitted H atoms), f_H the coherent scattering amplitude of H corrected for estimated thermal motion, and $P = 10$. This condition limited the included terms to those having a value greater than P for the ratio of probabilities of $F_o F_c > 0$ and $F_o F_c < 0$ (Woolfson, 1956).

Full-matrix least-squares refinement (program *XFLS4*) minimized the function $\sum w(F_o^2 - \gamma S^2 F_c^2)^2$ with $w = [\sigma_{\text{stat}}^2 + (0.03 F_o^2)^2]^{-1}$ where σ_{stat}^2 is the variance of F_o^2 computed from counting statistics. Extinction-correction factors γ were formulated after Coppens & Hamilton (1970), using the anisotropic type 1 form for the sulfate and the isotropic form for the borate. Atomic scattering factors from the 1972 *MIT* compilation (Koester, 1972) were used as follows, all in units of 10^{-13} cm : $f_B = 5.34$, $f_B'' = 0.21$, $f_H = -3.74$, $f_{Na} = 3.62$, $f_O = 5.803$, and $f_S = 2.847$. Final measures of disagreement, defined as in Thiessen, Levy & Flaig (1978), were:

	$R(F)$	$R(F^2)$	$R(wF^2)$	σ_1
Sulfate				
All reflections (2636)	0.153	0.099	0.120	1.083
$F^2 > \sigma(F^2)$ (1750)	0.087	0.082	0.098	1.144
Borate				
All reflections (2373)	0.094	0.067	0.089	1.027
$F^2 > \sigma(F^2)$ (1837)	0.061	0.060	0.078	1.045.

Sulfate: The initial observed Fourier synthesis and a difference synthesis disclosed peaks of negative density at all the H atom sites proposed by Ruben *et al.* (1961), including those suggested to be fractionally occupied in statistical disorder. Least-squares fitting of occupancy factors for the disordered sites yielded 0.50 with a standard deviation of 0.01 for each. Subsequently, these factors were fixed at exactly 0.5. Thus the equal populations of the various disordered arrangements of water molecules, deduced by Ruben *et al.* (1961) to explain the residual entropy (Pitzer & Coulter, 1938; Brodale & Giauque, 1958) of $R \ln 2$ gibbs mol^{-1} , are confirmed.†

Refinement proceeded normally, first with isotropic extinction factors fitted to averages of symmetry-equivalent structure factor squares, then with anisotropic extinction factors fitted to the individual values. Finally, with fixed scale and extinction parameters, structural parameters were fitted to averaged,

extinction-corrected data.* When refinement halted with measures of disagreement larger than usual satisfactory values, a difference Fourier synthesis was prepared which suggested an elaboration of the model for the sulfate ion – specifically two orientations differing by a rotation about one S–O bond direction. Accordingly, three O atoms [O(4), O(6), and O(7)] were replaced by two partially occupied sites each, as

* Fitting of scale and anisotropic extinction parameters was repeated near the end of the refinement sequence, but no significant changes occurred.

Table 1. Fractional atomic coordinates and site-occupancy parameters for sodium sulfate decahydrate

Least-squares standard errors in the final digits are given in parentheses.

	Occupancy	x	y	z
S(1)	1.000	0.2495 (6)	0.3601 (5)	0.2578 (4)
Na(2)	1.000	0.2547 (5)	0.7472 (7)	0.0145 (4)
Na(3)	1.000	0.2457 (5)	0.6126 (5)	0.7604 (4)
O(4')	0.247	0.2346 (16)	0.3368 (22)	0.3668 (13)
O(4'')	0.753 (15)	0.2636 (5)	0.2887 (7)	0.3603 (4)
O(5)	1.000	0.1438 (3)	0.3106 (4)	0.1718 (3)
O(6')	0.247	0.3598 (15)	0.2813 (22)	0.2546 (16)
O(6'')	0.753	0.3576 (4)	0.3443 (8)	0.2238 (4)
O(7')	0.247	0.2782 (17)	0.4955 (16)	0.2442 (14)
O(7'')	0.753	0.2298 (7)	0.4969 (5)	0.2748 (5)
O(8)	1.000	0.1233 (4)	0.4553 (5)	0.6403 (3)
O(9)	1.000	0.3672 (5)	0.4524 (5)	0.8784 (4)
O(10)	1.000	0.1018 (4)	0.3467 (5)	0.9456 (4)
O(11)	1.000	0.3967 (3)	0.3471 (4)	0.5799 (3)
O(12)	1.000	0.1131 (4)	0.6102 (5)	0.8778 (3)
O(13)	1.000	0.3880 (4)	0.6092 (5)	0.6498 (3)
O(14)	1.000	0.1459 (4)	0.7111 (4)	0.1435 (3)
O(15)	1.000	0.3547 (4)	0.7143 (4)	0.3782 (3)
O(16)	1.000	0.1310 (5)	0.5611 (5)	0.4423 (4)
O(17)	1.000	0.3798 (4)	0.5583 (5)	0.0812 (5)
H(8A)	1.000	0.1412 (7)	0.3645 (9)	0.6540 (5)
H(8B)	0.500	0.1376 (12)	0.4786 (16)	0.5698 (13)
H(8C)	0.500	0.0323 (18)	0.4529 (16)	0.6187 (12)
H(9A')	0.247	0.3588 (64)	0.1238 (89)	0.3515 (59)
H(9A'')	0.753	0.3335 (13)	0.1321 (15)	0.3687 (14)
H(9B)	0.500	0.4557 (20)	0.4428 (16)	0.8835 (13)
H(9C)	0.500	0.3669 (14)	0.4784 (17)	0.9535 (14)
H(10A)	1.000	0.1268 (6)	0.3348 (7)	0.0238 (6)
H(10B)	1.000	0.1495 (7)	0.2920 (8)	0.9153 (6)
H(11A)	1.000	0.3485 (6)	0.3329 (7)	0.5044 (5)
H(11B)	1.000	0.3691 (6)	0.2868 (8)	0.6235 (6)
H(12A)	1.000	0.1079 (6)	0.5240 (9)	0.9014 (5)
H(12B)	1.000	0.0300 (6)	0.6402 (8)	0.8509 (5)
H(13A)	1.000	0.3945 (6)	0.5238 (8)	0.6265 (6)
H(13B)	1.000	0.4725 (6)	0.6341 (8)	0.6861 (5)
H(14A)	1.000	0.0592 (7)	0.7017 (8)	0.1118 (5)
H(14B)	1.000	0.1707 (6)	0.6326 (8)	0.1801 (5)
H(15A)	1.000	0.3246 (6)	0.6333 (8)	0.3450 (5)
H(15B)	1.000	0.4431 (6)	0.7058 (8)	0.3990 (5)
H(16A')	0.247	0.1749 (63)	0.4897 (63)	0.4145 (52)
H(16A'')	0.753	0.1634 (15)	0.5210 (18)	0.3896 (14)
H(16B)	0.500	0.0437 (20)	0.5587 (15)	0.4053 (11)
H(16C)	0.500	0.1418 (14)	0.5091 (19)	0.5128 (15)
H(17A')	0.247	0.3569 (48)	0.5228 (53)	0.1587 (42)
H(17A'')	0.753	0.3633 (11)	0.4972 (17)	0.1314 (11)
H(17B)	0.500	0.3648 (12)	0.5124 (18)	0.0119 (19)
H(17C)	0.500	0.4713 (16)	0.5585 (17)	0.1084 (10)

* Computer programs used during this study are listed by Lisensky, Johnson & Levy (1976).

† 1 gibbs = 1 defined cal K^{-1} .

were three H atoms [H(9A), H(16A), and H(17A)] associated with three of the hydrogen bonds to these O atoms. This model was refined to the final result with one variable occupancy factor. Numerical stability was maintained by constraining the thermal parameters of the sites corresponding to the minor orientation (25% occupancy, singly primed symbols) to be isotropic.

Table 1 lists the final atomic coordinates.* Numbering of the heavy atoms conforms to that of Ruben *et al.* (1961). H atoms are labeled with the symbol $H\alpha\beta$, designating hydrogen atom β ($\beta = A, B, \text{ or } C$) bonded to O atom α ($8 \leq \alpha \leq 17$). A 'C' site is always statistically disordered with the corresponding B site. Primed and doubly primed symbols designate sites associated respectively with the minor and major orientations of the sulfate ion; the final value of the occupancy factor for the latter is 0.753 (15).

Borate: Least-squares refinement proceeded normally with only isotropic extinction corrections required and with no indication of disorder. Table 2 lists the atomic coordinates.* The atomic designations for Na, B, and O conform to those of Morimoto (1956), and those for H are similar to those described for the sulfate: $H\alpha\beta$ ($4 \leq \alpha \leq 9, \beta = A \text{ or } B$).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33712 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional atomic coordinates for sodium tetraborate decahydrate

Least-squares standard errors in the final digit are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
Na(1)	0	0	0
Na(2)	0	0.8469 (4)	0.2500
B(1)	0.0852 (1)	0.3452 (1)	0.2151 (1)
B(2)	0.0978 (1)	0.4566 (1)	0.3918 (1)
O(1)	0	0.2672 (2)	0.2500
O(2)	0.1544 (1)	0.4194 (1)	0.3146 (1)
O(3)	0.0194 (1)	0.4346 (1)	0.1243 (1)
O(4)	0.1614 (1)	0.2712 (2)	0.1679 (1)
O(5)	0.1622 (1)	0.5163 (2)	0.4895 (1)
O(6)	0.1240 (1)	0.8463 (2)	0.4493 (1)
O(7)	0.1233 (1)	0.0009 (2)	0.1956 (1)
O(8)	0.1197 (1)	0.1647 (2)	0.4615 (1)
O(9)	0.1171 (1)	0.7049 (2)	0.1718 (1)
H(4)	0.7616 (2)	0.2597 (3)	0.2807 (2)
H(5)	0.1127 (2)	0.4589 (3)	0.0379 (2)
H(6A)	0.3003 (3)	0.3857 (3)	0.0367 (3)
H(6B)	0.8662 (3)	0.2109 (3)	0.4875 (3)
H(7A)	0.2984 (2)	0.4755 (3)	0.3064 (3)
H(7B)	0.1276 (3)	0.0909 (3)	0.2021 (3)
H(8A)	0.9160 (3)	0.1958 (3)	0.1158 (3)
H(8B)	0.8064 (3)	0.1290 (5)	0.0364 (4)
H(9A)	0.4004 (4)	0.1177 (4)	0.3362 (4)
H(9B)	0.6152 (3)	0.2359 (4)	0.0967 (3)

Description and discussion

The cation chains of Na ions coordinated by bridging water molecules, extending parallel to *c*, are illustrated in Fig. 1(a) (sulfate) and (b) (borate), in which the structures are viewed perpendicular to the (100) plane. In this and subsequent drawings comparing the two structures, the view directions were chosen to display the similarity of configuration of the Na–water coordination chains. To achieve this objective, it was necessary to reverse the direction of one axis in the plane of each figure, as indicated in the figure captions. All such drawings are made with the same scale and are referred to a right-handed axial system.

In the sulfate, a glide plane relates adjacent equivalent atoms along the chain. In the borate structure the analogous glide plane is a consequence of centers of symmetry which occur at Na(1) and diad axes which occur at Na(2). In spite of the difference in crystallographic symmetry, the two chains are remarkably similar. In both chains, hydrogen bonds occur between adjacent non-bridging water molecules: in the sulfate, O(8)···H···O(16) and O(9)···H···O(17) with the H atom site disordered, and in the borate, O(9)–H···O(8) without disorder.

The configuration of chains relative to one another is illustrated in Fig. 2(a) (sulfate) and (b) (borate), in which the chains are viewed end-on (along *c**) and in which they form in section a centered nearly square net with anions occupying the edge midpoints. A pair of nearest-neighbor chains related to each other by inversion, corresponding to corner and center in Fig. 2(a) and (b), are shown viewed along *b* in Fig. 3(a) (sulfate) and (b) (borate) along with the outline of the cell edges. Here a principal difference between the two salts appears. Adjacent cation chains stack with opposite displacements parallel to the chain axis in such a way that interchain hydrogen bonds O(8)···H···O(16) and O(9)···H···O(17) (disordered H sites) are formed in the sulfate but not in the borate, where the atoms corresponding to the hydrogen-bonded pairs are O(8) and O(9). These displacements, though opposite in direction, are roughly equal in magnitude, namely about *c*/8, half the projected length of one Na coordination octahedron. In consequence, the β angles for the two salts are approximately equal in spite of the distinctly different packing arrangements.

Anions in the two salts form linear chains by hydrogen bonding and fill the channels at the edge midpoints of the nets described above. In the sulfate, adjacent SO_4^{2-} ions are glide-plane related and are bridged by two water molecules [O(10) and O(11)] not involved in the cation chains. Hydrogen bonds link the sulfate O atoms and the water molecules which bridge them with the water molecules of the cation chains. These aspects of the structure appear in Fig. 4(a) (viewed along *b*) and in Fig. 1(a) (viewed along *a**).

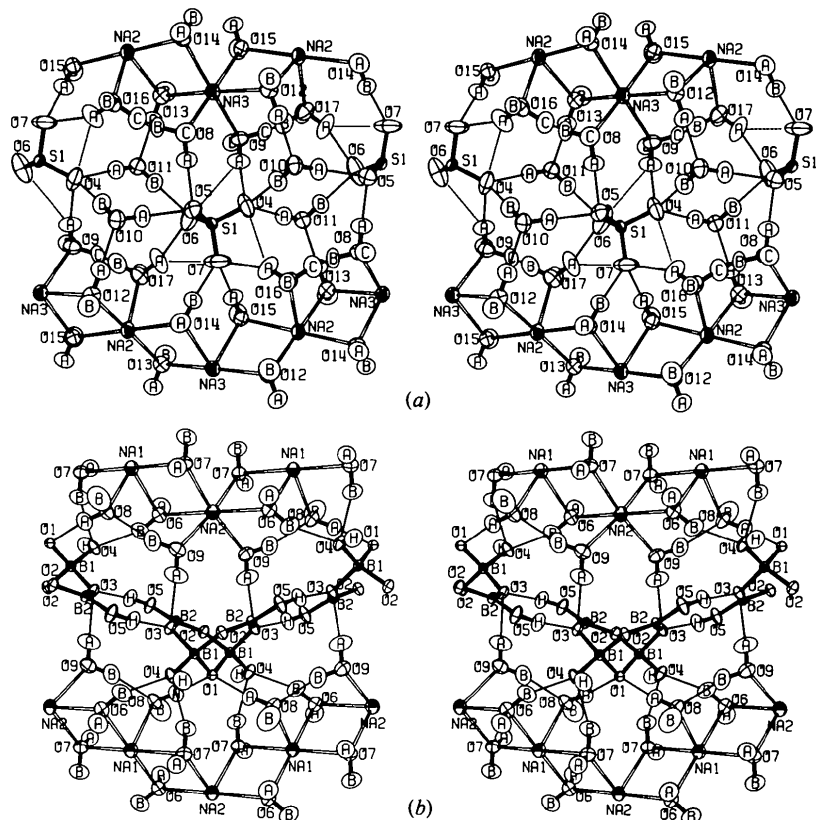


Fig. 1. (a) Sodium sulfate and (b) borax structures viewed perpendicular to the (100) plane. The c axis is horizontal, left to right. The b axis is vertical, upward in the sulfate and downward in the borate.

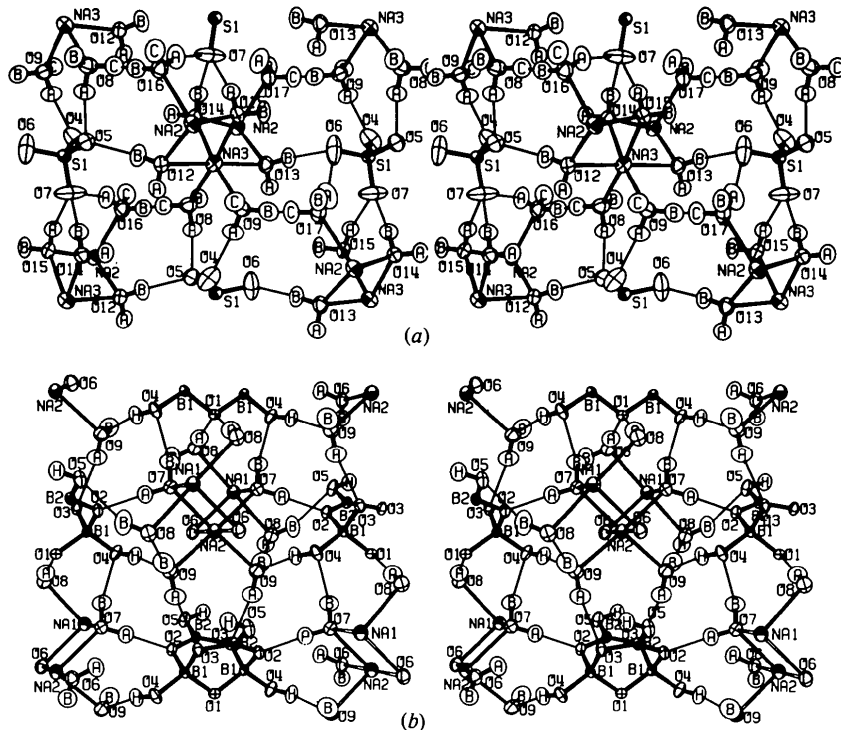


Fig. 2. (a) Sodium sulfate and (b) borax structures viewed perpendicular to the (001) plane. The b axis is vertical, upward, in both figures. The a axis is horizontal, left to right in the sulfate, and right to left in the borate.

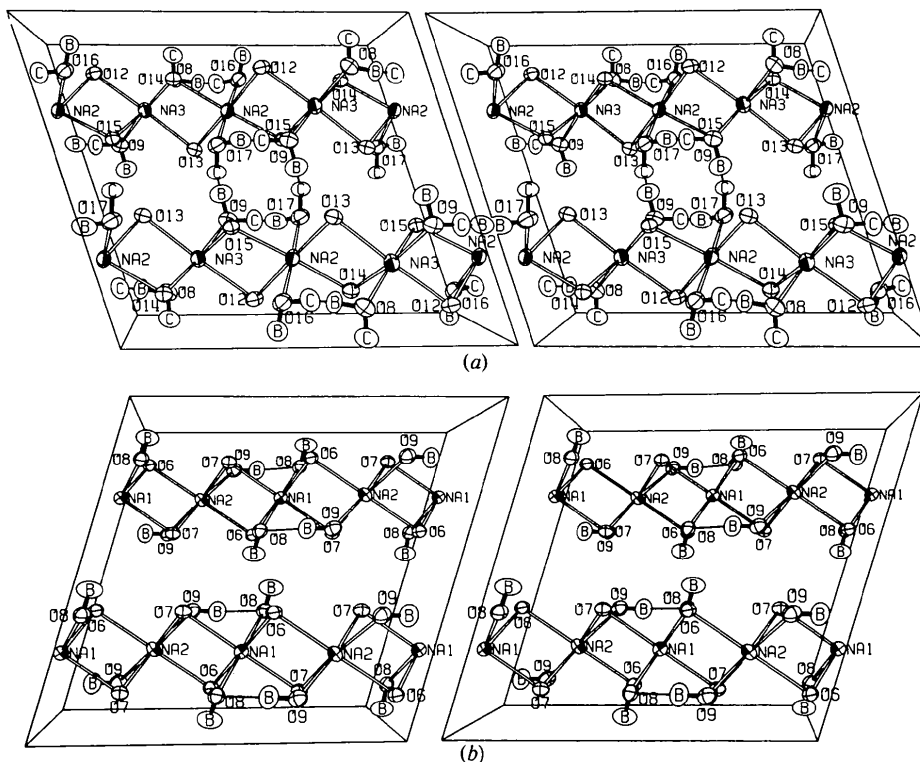


Fig. 3. The configurations of adjacent sodium ion coordination chains in (a) sodium sulfate and (b) borax. The view direction is along the b axis. The c axis is horizontal, left to right, and the a axis points upward for the sulfate and downward for the borate. Some hydrogen atoms have been omitted for clarity. The cell outline is centered on the inversion point ($\frac{1}{2}, \frac{1}{2}, 0$) for the sulfate and on the inversion point ($\frac{1}{3}, \frac{1}{3}, 0$) for the borate.

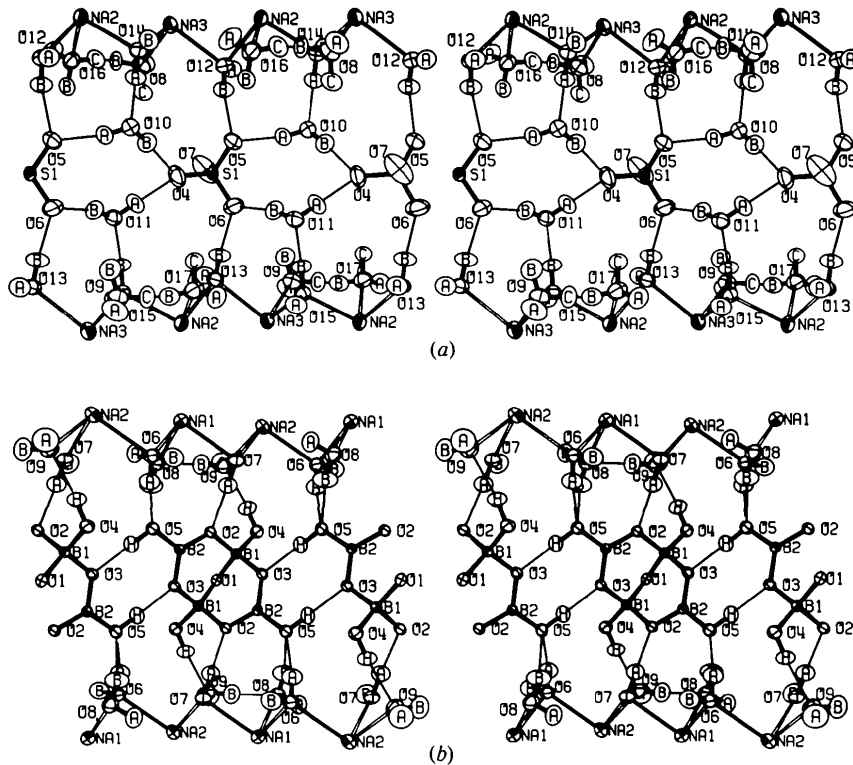


Fig. 4. (a) Sodium sulfate and (b) borax structures viewed along the b axis, with the c axis horizontal, left to right. The a axis is upward in the sulfate, downward in the borate.

Table 3. Distances (Å) and angles (°) in sodium sulfate decahydrate

Sodium ion coordination chain					
Na(3)—O(8)	2.385 (7)	Na(2)—O(12)	2.450 (7)		
—O(9)	2.389 (7)	—O(13)	2.440 (7)		
—O(12)	2.450 (6)	—O(14)	2.390 (6)		
—O(13)	2.474 (6)	—O(15)	2.402 (6)		
—O(14)	2.420 (6)	—O(16)	2.454 (8)		
—O(15)	2.432 (7)	—O(17)	2.425 (8)		
O(12)—Na(2)—O(13)	177.3 (4)	O(8)—Na(3)—O(13)	89.0 (2)		
—O(14)	91.8 (2)	—O(14)	92.3 (2)		
—O(15)	86.3 (2)	—O(15)	174.9 (3)		
—O(16)	91.0 (3)	O(9)—Na(3)—O(12)	87.5 (2)		
—O(17)	88.7 (3)	—O(13)	89.6 (2)		
O(13)—Na(2)—O(14)	87.1 (2)	—O(14)	172.9 (3)		
—O(15)	94.7 (2)	—O(15)	91.6 (3)		
—O(16)	86.6 (3)	O(12)—Na(3)—O(13)	176.9 (3)		
—O(17)	93.7 (3)	—O(14)	97.1 (2)		
O(14)—Na(2)—O(15)	177.2 (3)	—O(15)	85.7 (2)		
—O(16)	91.3 (3)	O(13)—Na(3)—O(14)	85.8 (2)		
—O(17)	90.5 (3)	—O(15)	93.5 (2)		
O(15)—Na(2)—O(16)	86.7 (2)	O(14)—Na(3)—O(15)	83.4 (2)		
—O(17)	91.6 (3)	Na(2)—O(12)—Na(3)	91.8 (2)		
O(16)—Na(2)—O(17)	178.2 (3)	—O(13)—	91.0 (2)		
O(8)—Na(3)—O(9)	92.9 (3)	—O(14)—	93.6 (2)		
—O(12)	92.1 (3)	—O(15)—	93.4 (2)		
Sulfate ion					
	(Corrected) ^a		(Corrected) ^a		
S(1)—O(5)	1.463 (7)	1.481 (7)	S(1)—O(4')	1.48 (2)	1.49 (2)
S(1)—O(4'')	1.475 (6)	1.487 (6)	—O(6')	1.52 (2)	1.54 (2)
—O(6'')	1.447 (7)	1.467 (7)	—O(7')	1.46 (2)	1.47 (2)
—O(7'')	1.463 (7)	1.486 (7)			
O(5)—S(1)—O(4'')	109.7 (4)		O(5)—S(1)—O(4')	110.3 (7)	
—O(6'')	109.0 (4)		—O(6')	107.4 (7)	
—O(7'')	108.7 (5)		—O(7')	114.3 (7)	
O(4'')	S(1)—O(6'')	110.0 (5)	O(4')—S(1)—O(6')	106.0 (10)	
—O(7'')	109.4 (5)		—O(7')	111.4 (10)	
O(6'')	S(1)—O(7'')	110.0 (5)	O(6')—S(1)—O(7')	106.9 (11)	
Non-disordered water bond angles (°)					
O(10)	108.9 (7)	O(11)	107.1 (7)	O(12)	105.4 (7)
O(13)	103.7 (7)	O(14)	103.9 (7)	O(15)	104.4 (7)

(a) Corrected for the effect of thermal motion, by means of the riding model (*International Tables for X-ray Crystallography*, 1974).

chains is by means of shared edges, supplemented by hydrogen bonds between pairs of non-bridging water molecules on neighboring octahedra. The chains are zig-zag in the (100) plane [see bottom part of Fig. 1(a) and (b)] with a vertex at alternate sodium ions [Na(2) in the borate and Na(3) in the sulfate], at which the two octahedral edges shared with neighbors are non-parallel, in contrast to the remaining octahedra where the shared edges are opposite and nearly parallel. There is also a smaller bend in the chain at each shared edge, since adjacent octahedra are tilted out of the parallel configuration. In part, this tilt is to accommodate the intrachain hydrogen bonds, which are shorter (2.8–2.9 Å) than the distance between octahedral centers (3.46–3.52 Å); these tilt angles are 15.32 (11)° and 15.93 (11)° in the sulfate and 2.13 (5)° in the borate, as measured by the dihedral angle between planes fitted to the Na ion and the square of O atoms built upon the

Table 4. Distances (Å) and angles (°) in sodium tetraborate decahydrate

Sodium ion coordination chain					
Na(1)—O(6)	2.399 (2)	Na(2)—O(6)	2.458 (2)		
—O(7)	2.418 (2)	—O(7)	2.415 (3)		
—O(8)	2.388 (2)	—O(9)	2.428 (3)		
O(6)—Na(1)—O(7)	89.50 (5)	O(6)—Na(2)—O(9)	97.97 (9)		
—O(8)	89.63 (6)	O(7)—Na(2)—O(7)	94.46 (15)		
O(7)—Na(1)—O(8)	88.30 (5)	—O(9)	81.63 (6)		
O(6)—Na(2)—O(6)	179.68 (21)	—O(9)	172.77 (10)		
—O(7)	88.21 (8)	O(9)—Na(2)—O(9)	102.89 (17)		
—O(7)	92.00 (8)	Na(1)—O(6)—Na(2)	90.86 (8)		
—O(9)	81.83 (7)	Na(1)—O(7)—Na(2)	91.44 (5)		
Borate ion					
B(1)—O(1)	1.464 (2)	B(2)—O(2)	1.363 (2)		
—O(2)	1.485 (2)	—O(3)	1.370 (2)		
—O(3)	1.500 (2)	—O(5)	1.374 (2)		
—O(4)	1.440 (2)				
O(1)—B(1)—O(2)	109.39 (10)	O(2)—B(2)—O(5)	118.20 (11)		
—O(3)	108.52 (10)	O(3)—B(2)—O(5)	119.61 (11)		
—O(4)	111.85 (12)	B(1)—O(4)—H(4)	113.60 (20)		
O(2)—B(1)—O(3)	108.39 (11)	B(2)—O(5)—H(5)	111.51 (20)		
—O(4)	110.75 (11)	B(1)—O(2)—B(2)	116.93 (10)		
O(3)—B(1)—O(4)	107.85 (11)	B(1)—O(3)—B(2)	120.56 (11)		
O(2)—B(2)—O(3)	122.19 (11)	B(1)—O(1)—B(1)	110.81 (15)		
Water molecule bond angles (°)					
O(6)	103.9 (3)	O(7)	104.4 (3)	O(8)	107.7 (4)
		O(9)	106.8 (4)		

shared edge. The sense of this bend is opposite to that at Na(2) (borate) and Na(3) (sulfate) and thus tends to straighten the chain and to lengthen the *c* axis repeat distance. The considerably smaller tilt angle in the borate cation chain is only partly a consequence of the longer hydrogen bond; it results mostly from a sizeable distortion of the Na(2) octahedron away from regularity. Thus the O(9)—Na(2)—O(9) angle (Table 4) is 102.9°, much greater than 90°, the value for a regular octahedron. The small tilt angle in the borate is correlated with the shorter *c* axis repeat distance. Presumably this configuration best accommodates the hydrogen bonds between the cation and anion chains.

In each structure there are a total of 20 hydrogen bonds per formula unit, of which two are within the cation chains. In the borate, two hydrogen bonds link the anions and 16 interconnect cation chains with anions. In the sulfate, the bridging of anions by water molecules accounts for four hydrogen bonds, the interaction of adjacent cation chains accounts for two, and the remaining 12 interconnect cation chains with anions or anion-bridging water molecules. As judged by interatomic distances, there is no great variation in bond strength, except perhaps for the O(5)—H...O(3) bond in the borate, which is the shortest; however, the borate arrangement, having more links between cation and anion entities, is the more favorable and accounts for the greater stability of borax against dehydration.

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Table 5. *Hydrogen bonds in Na₂SO₄·10H₂O*

Identification ^a			Type ^b	Distance (Å)			Angle (°)	
				Uncorrected	Corrected ^c	H...O		O...O
α	β	γ		O—H	O—H	H...O	O...O	O—H...O
Between singly coordinated water molecules in the same chain								
8	B	16	W(1)—W(1)	1.00 (2)	1.02 (2)	1.83 (2)	2.79 (1)	162.3 (14)
16	C	8	W(1)—W(1)	1.03 (2)	1.06 (2)	1.80 (2)		161.0 (16)
9	C	17	W(1)—W(1)	1.00 (2)	1.03 (2)	1.80 (2)	2.79 (1)	167.3 (15)
17	B	9	W(1)—W(1)	0.98 (3)	0.99 (3)	1.83 (3)		165.7 (14)
Between singly coordinated water molecules in adjacent chains								
8	C	16	W(1)—W(1)	1.00 (2)	1.02 (2)	1.81 (2)	2.80 (1)	170.4 (13)
16	B	8	W(1)—W(1)	0.97 (2)	0.98 (2)	1.83 (2)		169.5 (12)
9	B	17	W(1)—W(1)	1.00 (2)	1.03 (2)	1.81 (2)	2.80 (1)	168.5 (14)
17	C	9	W(1)—W(1)	1.00 (2)	1.02 (2)	1.81 (2)		165.3 (12)
Between doubly coordinated water and uncoordinated water								
12	A	10	W(2)—W	0.95 (1)	0.97 (1)	1.93 (1)	2.88 (1)	177.6 (6)
13	A	11	W(2)—W	0.94 (1)	0.96 (1)	1.93 (1)	2.87 (1)	176.0 (6)
14	A	10	W(2)—W	0.96 (1)	0.98 (1)	1.84 (1)	2.79 (1)	170.0 (8)
15	B	11	W(2)—W	0.97 (1)	1.00 (1)	1.86 (1)	2.82 (1)	166.3 (7)
Between water and sulfate oxygen, common orientation								
8	A	5	W(1)—O	0.97 (1)	0.99 (1)	1.83 (1)	2.78 (1)	169.3 (7)
10	A	5	W—O	0.96 (1)	0.98 (1)	1.87 (1)	2.82 (1)	169.2 (6)
12	B	5	W(2)—O	0.96 (1)	1.00 (1)	2.00 (1)	2.94 (1)	167.0 (6)
Between water and sulfate oxygen, major orientation								
10	B	4''	W—O	0.95 (1)	0.97 (1)	1.87 (1)	2.81 (1)	169.1 (8)
11	A	4''	W—O	0.97 (1)	0.99 (1)	1.87 (1)	2.83 (1)	174.1 (7)
9	A''	4''	W(1)—O	0.95 (2)	0.97 (2)	1.80 (2)	2.75 (1)	174.7 (17)
11	B	6''	W—O	0.96 (1)	0.98 (1)	1.90 (1)	2.84 (1)	165.2 (6)
13	B	6''	W(2)—O	0.98 (1)	1.00 (1)	1.96 (1)	2.92 (1)	169.2 (8)
17	A''	6''	W(1)—O	0.96 (1)	0.99 (2)	1.99 (2)	2.94 (1)	166.0 (16)
14	B	7''	W(2)—O	0.94 (1)	0.96 (1)	1.85 (1)	2.78 (1)	169.5 (6)
15	A	7''	W(2)—O	0.96 (1)	0.98 (1)	1.84 (1)	2.78 (1)	165.9 (7)
16	A''	7''	W(1)—O	0.96 (2)	0.98 (2)	1.87 (2)	2.80 (1)	161.8 (18)
Between water and sulfate oxygen, minor orientation								
10	B	4'	W—O	0.95 (1)	0.97 (1)	1.87 (2)	2.81 (2)	170.9 (10)
11	A	4'	W—O	0.97 (1)	0.99 (1)	1.85 (2)	2.80 (2)	166.5 (10)
16	A'	4'	W(1)—O	1.01 (7)	1.05 (7)	1.90 (8)	2.91 (2)	169.6 (62)
11	B	6'	W—O	0.96 (1)	0.98 (1)	1.86 (2)	2.75 (2)	154.1 (10)
13	B	6'	W(2)—O	0.98 (1)	1.00 (1)	2.04 (2)	3.01 (2)	168.9 (10)
9	A'	6'	W(1)—O	0.86 (9)	0.90 (9)	2.05 (9)	2.88 (3)	163.1 (6)
14	B	7'	W(2)—O	0.94 (1)	0.96 (1)	1.90 (2)	2.79 (2)	157.4 (9)
15	A	7'	W(2)—O	0.96 (1)	0.98 (1)	1.89 (2)	2.82 (2)	162.7 (8)
17	A'	7'	W(1)—O	1.16 (6)	1.18 (6)	1.64 (6)	2.77 (2)	159.7 (44)

(a) The symbol ($\alpha\beta\gamma$) designates the hydrogen bond $O_{\alpha}-H_{\alpha\beta}\cdots O_{\gamma}$.

(b) The symbol W(1) denotes 'terminal' water coordinated to only one Na⁺ ion, W(2) denotes bridging water coordinated to two Na⁺ ions, W denotes water not coordinated to Na⁺ ions, and O denotes sulfate oxygen.

(c) Corrected for the effect of thermal motion by means of the riding model (*International Tables for X-ray Crystallography*, 1974).

Table 6. *Hydrogen bonds in borax*

Identification ^a			Type ^b	Distance (Å)			Angle (°)	
				Uncorrected	Corrected ^c	H...O		O...O
α	β	γ		O—H	O—H	H...O	O...O	O—H...O
4		9	OH, W(1)	0.958 (3)	0.974 (3)	1.937 (3)	2.883 (2)	168.9 (3)
5		3	OH, O	0.982 (3)	0.991 (3)	1.755 (3)	2.731 (2)	172.8 (3)
6	A	5	W(2), OH	0.963 (3)	0.984 (3)	1.891 (3)	2.842 (2)	168.6 (3)
6	B	4	W(2), OH	0.964 (4)	0.985 (4)	1.940 (4)	2.865 (2)	160.1 (3)
7	A	2	W(2), O	0.976 (3)	0.991 (3)	1.843 (3)	2.818 (2)	176.7 (3)
7	B	4	W(2), OH	0.962 (4)	0.988 (4)	2.031 (4)	2.950 (2)	159.2 (3)
8	A	1	W(1), O	0.975 (3)	0.986 (3)	1.823 (3)	2.790 (2)	170.4 (3)
8	B	5	W(1), OH	0.951 (4)	0.998 (4)	2.259 (4)	3.148 (2)	155.4 (4)
9	A	3	W(1), O	0.951 (4)	0.986 (4)	2.164 (4)	3.097 (2)	166.6 (4)
9	B	8	W(1), W(1)	0.969 (4)	0.996 (4)	1.974 (4)	2.927 (2)	167.2 (4)

(a) The symbol ($\alpha\beta\gamma$) designates the hydrogen bond $O_{\alpha}-H_{\alpha\beta}\cdots O_{\gamma}$.

(b) The symbol OH denotes terminal hydroxide ion in the anion, O bridging oxygen in the anion, W(1) terminal water coordinated to one Na⁺ ion, and W(2) bridging water coordinated to two Na⁺ ions.

(c) Corrected for the effect of thermal motion by means of the riding model (*International Tables for X-ray Crystallography*, 1974).

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Structure d'Hydrogéoorthophosphates de Thallium(I).

I. Structure du Pentahydrogéoorthophosphate de Thallium(I) $\text{TlH}_5(\text{PO}_4)_2$

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The crystals of $\text{TlH}_5(\text{PO}_4)_2$ are monoclinic ($C2/c$) with cell parameters $a = 10.307$ (3), $b = 7.748$ (2), $c = 9.609$ (3) Å and $\beta = 100.80$ (3)°, $Z = 4$. The crystal structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations to $R = 0.038$ on the 876 independent reflexions measured. The structure is different from $\text{KH}_5(\text{PO}_4)_2$; the Tl^+ ion is six-coordinated while the K^+ ion is eight-coordinated. In the case of $\text{TlH}_5(\text{PO}_4)_2$ the short hydrogen bond (2.43 Å) is necessarily symmetric.

Introduction

La détermination de la structure cristalline de $\text{TlH}_4(\text{PO}_4)_2$ par diffraction de rayons X entre dans le cadre d'une étude systématique effectuée au laboratoire sur les hydrogéoorthophosphates de thallium(I) en tant qu'hydrogénocomposés.

La préparation de ce sel de thallium a été conduite à partir de l'étude du diagramme de solubilité ternaire ($\text{H}_2\text{O}-\text{H}_3\text{PO}_4-\text{TlH}_2\text{PO}_4$) à 25°C (Oddon, Boiron & Tranquard, 1975). Des cristaux en forme d'aiguille (4 à 5 mm de long, 0.2 mm de diamètre) translucides et incolores sont ainsi obtenus dans le domaine d'existence de la phase $\text{TlH}_5(\text{PO}_4)_2$.

Ce travail a été entrepris dans le but de mieux connaître l'ion Tl^+ déjà étudié dans un certain nombre d'autres composés. Une analyse comparative de la structure de $\text{TlH}_5(\text{PO}_4)_2$ avec celle d'un composé isotype $\text{KH}_5(\text{PO}_4)_2$ (Philippot & Lindqvist, 1971;

Philippot, Richard, Roudault & Maurin, 1972) permettra de voir les modifications structurales résultant du remplacement de l'ion alcalin K^+ par l'ion Tl^+ présentant un rayon ionique du même ordre de grandeur [1,40 Å pour Tl^+ et de 1,33 Å pour K^+ (Pauling, 1960)].

Données expérimentales

Les études radiocristallographiques préliminaires effectuées sur chambre de précession ont mis en évidence l'absence systématique des réflexions du type $h + k = 2n + 1$ sur hkl et des réflexions du type $l = 2n + 1$ sur $h0l$; les groupes d'espace Cc et $C2/c$ répondent à ces extinctions. Les affinements effectués ultérieurement attestent la présence d'un centre de symétrie, le sel appartient donc au groupe spatial $C2/c$. Les mesures d'intensité des réflexions ont été effectuées sur diffracto-