

made between 3.10 and 3.11 Å (as was done for β -Pu) the results are as shown in Table 3. Disregarding Pu(1), which is probably Zr, the average number of short bonds is three.

Zachariassen (1973) has discussed the radii of Pu and other actinide elements in their various phases and deduced the number of valence electrons. He defines the radius as $r = V_a^{1/3}/2^{5/6}$ where V_a is the mean atomic volume. For the present material $V_a = 22.42 \text{ \AA}^3$, $r = 1.583 \text{ \AA}$ and the mean valence is therefore 5.2 electrons. This value is the same as that of γ -Pu.

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Hydrogen Bonds in Schlippe's Salt: Refinement of the Crystal Structures of $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ by X-ray Diffraction and $\text{Na}_3\text{SbS}_4 \cdot 9\text{D}_2\text{O}$ by Neutron Diffraction at Room Temperature

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Abstract

The room-temperature crystal structure of Schlippe's salt, space group $P2_13$, $Z = 4$, has been refined for $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$, $a = 11.957(3) \text{ \AA}$, from X-ray data to $R_F = 0.022$, and for $\text{Na}_3\text{SbS}_4 \cdot 9\text{D}_2\text{O}$, $a = 11.959(3) \text{ \AA}$, from neutron data to $R_F = 0.058$. X-ray and neutron results are in good agreement. Within experimental error, no structural isotope effect between the H and D compounds is observed. Finite groups of

distorted, face-sharing Na coordination octahedra, $[(\text{H}_2\text{O})_3\text{Na}(\text{H}_2\text{O})_3\text{Na}(\text{H}_2\text{O})_3\text{NaS}_3]$ (point symmetry 3), and SbS_4 tetrahedra (point symmetry 3) share common corners *via* three of their four S atoms to form a three-dimensional framework. Average bond lengths are $\text{Na}-\text{O} = 2.39$, $\text{Na}-\text{S} = 3.00$, $\text{Sb}-\text{S} = 2.33 \text{ \AA}$. D_2O molecules with $\text{D}-\text{O} = 0.93-0.97 \text{ \AA}$ and $\text{D}-\text{O}-\text{D} = 107-108^\circ$ form an extensive hydrogen-bond system. Six different bonds are observed: one $\text{O}-\text{D}\cdots\text{O}$ ($\text{O}\cdots\text{O} = 2.81 \text{ \AA}$), four approximately linear

O—D...S (O...S = 3.29–3.36, D...S = 2.34–2.40 Å); the sixth D atom forms a bifurcated bond with two S atoms [D(6)...S = 2.83 and 2.86 Å]. According to Raman spectra, all D as well as H atoms are involved in hydrogen bonding.

Introduction

The purpose of this work is to better characterize OH...S bonds. Schlippe's salt was chosen from several hydrated salts containing OH...S bonds for a more detailed study. The structure, without the H-atom positions, has already been described by Grund & Preisinger (1950), the isotope effect of several physical properties of Na₃SbS₄·9H₂O and Na₃SbS₄·9D₂O by Haussühl (1970), and the Raman spectrum of Na₃SbS₄·9H₂O single crystals by Claus (1970).

For structure refinement single-crystal X-ray diffraction intensities of Na₃SbS₄·9H₂O and single-crystal neutron diffraction intensities of Na₃SbS₄·9D₂O were measured. Further, Raman measurements in the temperature range 75 to 295 K were made on both compounds (Mikenda & Preisinger, 1978). ¹H NMR measurements were also performed.

X-ray diffraction measurements and refinement

The crystal data are summarized in Table 1. The cell parameters of both H and D compounds were determined by powder diffraction with α -quartz ($a = 4.913$, $c = 5.405$ Å; Swanson, Fuyat & Ugrinic, 1954) as internal standard. Commercially available Na₃SbS₄·9H₂O (Schuchardt, Munich) was recrystallized from water. A good-quality single crystal, laevorotatory for Na_D light, was ground to a sphere of radius 0.16 mm. Intensities were measured on a Stoe-Stadi-2 two-circle diffractometer in ω -scan mode with graphite-monochromatized Mo K α radiation. About

Table 1. *Crystal data for Schlippe's salt at room temperature*

Numbers in parentheses here and throughout the paper give the e.s.d.'s of the last significant digits.

	Na ₃ SbS ₄ ·9H ₂ O	Na ₃ SbS ₄ ·9D ₂ O	
	Space group $P2_13$, $Z = 4$		
a	11.957 (3) Å	11.959 (3) Å	(This paper)
	11.957 (2)	11.961 (2)	(Haussühl, 1970)
V	1709.5 Å ³	1710.4 Å ³	
D_m	1.870 (1) Mg m ⁻³	1.938 (1) Mg m ⁻³	(Haussühl, 1970)
D_c	1.870	1.939	
Linear absorption coefficients			
	Mo K α radiation 2.19 mm ⁻¹		
	Neutron radiation 0.0061 mm ⁻¹		

1600 reflections with $h, k \geq 0$, $0 \leq l \leq 9$ were measured. After correction for Lorentz, polarization and absorption effects, equivalent reflections were averaged. The resulting data set consisted of all 946 symmetry-independent reflections with $(\sin \theta)/\lambda < 0.703$ Å⁻¹. The 757 with $F_o^2 > 3\sigma(F_o^2)$ were considered as observed and were used in the subsequent calculations.

Full-matrix least-squares refinement started with the atomic positions given by Grund & Preisinger (1950) and converged with anisotropic temperature factors to $R_F = \sum (|F_o| - |F_c|)/\sum F_o = 0.043$. Refinement with an anomalous dispersion correction and with opposite absolute configurations of the structure led to $R = 0.032$ (x, y, z coordinate set) and $R = 0.026$ ($\bar{x}, \bar{y}, \bar{z}$ coordinate set). The absolute configuration $\bar{x}, \bar{y}, \bar{z}$ was further confirmed by a comparison of calculated and observed intensities of Friedel-pair reflections from Cu K α Weissenberg photographs of the same crystal sphere. (Since Bijvoet ratios are considerably larger for Cu K α radiation than for Mo K α , intensity differences are more easily recognized on the Cu K α photographs.)

The positions of all H atoms were taken from a difference synthesis. Refinement including the H atoms converged to $R = 0.023$ and gave O—H bond distances

Table 2. *Atomic coordinates* (-1×10^5 for Na, Sb, S, O, D; -1×10^4 for H; the minus sign in both factors refers to a laevorotatory crystal) and B_{eq} (Å²)

The X-ray values are listed above the neutron values.

	x	y	z	B_{eq}
Na(1)	29170 (12)	—	—	2.72
	29112 (32)			2.48
Na(2)	44999 (12)	—	—	2.59
	45011 (33)			2.38
Na(3)	60606 (13)	—	—	2.67
	60663 (35)			2.64
Sb	03724 (2)	—	—	1.77
	03712 (20)			2.00
S(1)	92492 (8)	—	—	3.17
	92459 (51)			3.43
S(2)	14848 (8)	14805 (8)	92188 (8)	2.36
	14788 (40)	14816 (44)	92282 (43)	2.36
O(1)	-02612 (27)	36709 (21)	92575 (23)	2.91
	-02686 (26)	36642 (23)	92610 (23)	2.76
O(2)	18387 (26)	69538 (25)	99246 (23)	3.21
	18445 (27)	69541 (24)	99294 (23)	2.97
O(3)	10119 (24)	25617 (28)	32875 (29)	3.49
	10074 (27)	25593 (27)	32853 (29)	3.29
H(1)	0246	3049	9276	3.2
D(1)	02163 (29)	30189 (25)	92121 (28)	4.00
H(2)	-0719	3598	8602	3.2
D(2)	-07326 (28)	36684 (26)	86187 (27)	3.87
H(3)	2515	6614	0193	3.2
D(3)	25114 (32)	66185 (31)	02221 (31)	4.57
H(4)	1665	7573	0405	3.2
D(4)	16799 (29)	75864 (27)	03976 (27)	4.18
H(5)	0553	2304	2681	3.2
D(5)	05069 (31)	22681 (37)	27323 (36)	5.12
H(6)	0593	3107	3702	3.2
D(6)	06031 (48)	30690 (34)	37063 (56)	7.47

of 0.70–0.84 Å, H–O–H angles of 93–102° and isotropic temperature factors for H of $B = 0.1\text{--}5.5 \text{ \AA}^2$. Much more realistic nuclear H positions were obtained by the refinement of rigid H₂O molecules. The following geometry for the water molecules was adopted and kept constant throughout the further refinement: inter-nuclear O–H distance 0.96 Å and H–O–H bond angle 108° (both values according to the geometry of the average water molecule of Ferraris & Franchini-Angela, 1972). A spherical scattering function was used for the H atoms. To account for the non-spherical scattering of bonded H atoms (Coppens, 1972), the scattering centers were placed not on the nuclear H positions but on the O–H lines 0.80 Å away from the O atoms (X-ray coordinates and distances of the H atoms given in the tables refer to nuclear H positions). The isotropic temperature factors of the H atoms were arbitrarily fixed at $B = 3.2 \text{ \AA}^2$.

In the final full-matrix least-squares refinement a scale factor, an extinction parameter and all atomic parameters were allowed to vary. The structure factors were corrected for extinction by $F_c^* = F_c(1 + 2r^* \delta F_c^2)^{-1/4}$ (Larson, 1970; the lowest extinction correction factor was 0.82) and were weighted by $\omega = 1/[\sigma^2(F_o) + 0.0004 F_o^2]$. The final $R_F = 0.022$ ($R_{F_w} = 0.018$) and $S = [\sum \omega(|F_o| - |F_c|)^2 / (757 - 52)]^{1/2} = 0.89$ (observed reflections only). Final atomic coordinates are given in Table 2.† Scattering factors for neutral atoms and anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). Computer programs from KM were used.

Neutron diffraction measurements and refinement

A crystal of Na₃SbS₄·9D₂O was cut to a {100} cube with an edge length of 4 mm. The crystal was dipped in liquid nitrogen to reduce extinction effects and then mounted on the automatic four-circle neutron diffractometer P110 at the research reactor FR2, Kernforschungszentrum Karlsruhe. A mean neutron wavelength $\lambda_N = 0.926 \text{ \AA}$ was used. The intensities of about 2400 reflections with $h, k, l \geq 0$ and $(\sin \theta)/\lambda < 0.694 \text{ \AA}^{-1}$ were measured with an ω scan. The data were corrected for the Lorentz effect but not for absorption ($\mu r \sim 0.01$). Equivalent reflections were averaged and resulted in a data set of 912 symmetry-independent reflections.

Full-matrix least-squares refinement started with the parameters from the X-ray refinement. The following

scattering lengths from Willis (1973) were used: 0.362 (Na), 0.564 (Sb), 0.2847 (S), 0.580 (O) and 0.667 (D) (all values $\times 10^{-14} \text{ m}$). For Schlippe's salt anomalous dispersion effects in neutron diffraction can be ignored. Atomic coordinates and anisotropic temperature factors as well as a scale factor and an extinction parameter were refined simultaneously. The structure factors were corrected for extinction with the same expression as for the X-ray data; the lowest extinction correction factor was 0.87. Unit weights were used except for the 38 very weak reflections which were given zero weight. The final $R_F = 0.058$ ($R_{F_w} = 0.058$) for 912 reflections. The final atomic coordinates are given in Table 2.* Computer programs of the XRAY system (Stewart, 1976) were used.

Comparison of X-ray and neutron results

The cell parameter of the D compound is larger than that of the H compound (Table 1) but not significantly so: the difference is 0.002 (4) Å in this work and 0.004 (3) Å in Haussühl (1970). Similar small differences, also hardly significant, have been observed between some H and D alums (Haussühl, 1961).

Apart from the coordinates of the H atoms (see below), the X-ray results are more precise for Na, Sb and S than the neutron results, and nearly as precise for the O atoms. The coordinates of the non-hydrogen atoms are in good agreement for both refinements. The differences between equivalent atomic coordinates divided by their pooled standard deviations, $\sigma_p = \sigma_X + \sigma_N$, are on average 0.85 and do not exceed 1.85. Distances between equivalent X and N positions vary from 0.002 to 0.013 Å with a mean of 0.008 Å. X-ray and neutron diffraction determined bond distances (Table 3) agree within 0.013 Å, that is, within 1.5 pooled standard deviations. Taking into account that least-squares standard deviations are usually an underestimate of the true error, the X-ray and neutron diffraction structures of Schlippe's salt do not differ significantly with respect to the atomic coordinates and the bond distances of the non-hydrogen atoms. This indicates that any isotope effect between the H and D forms of Schlippe's salt must be low or even zero. This agrees with the results of a neutron diffraction study of CuSO₄·5H₂O and CuSO₄·5D₂O by Bacon & Titterton (1975) who concluded that the isotope effect is negligible for this pair of salts as far as cell parameters, atomic coordinates and bond distances are concerned.

The positions of the D atoms have been determined by neutron diffraction to a precision better than 0.01 Å. The nuclear positions of the H atoms, which were obtained by refining rigid H₂O molecules with X-ray data, are of course less precise; however, this refine-

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33869 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See previous footnote.

ment method gave encouraging results: The assumed H_2O differs from the D_2O molecules actually found by $<1.3^\circ$ in the $\text{H}-\text{O}-\text{H}$ angle and $<0.033 \text{ \AA}$ in the $\text{O}-\text{H}$ distance. All nuclear H positions deviate from the corresponding D positions by $<0.1 \text{ \AA}$, on average only 0.06 \AA .

Description and discussion of the structure

SbS_4 tetrahedra and $\text{Na}(3)$ ions form a three-dimensional framework, where each SbS_4 tetrahedron is connected to three $\text{Na}(3)$ and each $\text{Na}(3)$ to three SbS_4 groups. The distorted octahedral coordination around $\text{Na}(3)$ is completed through three water molecules $\text{H}_2\text{O}(1)$ from a $\{[\text{H}_2\text{O}(3)]_3\text{Na}(1)[\text{H}_2\text{O}(2)]_3\text{Na}(2)-[\text{H}_2\text{O}(1)]_3\}$ group. Through a system of hydrogen bonds, the water molecules contribute much to the stability of the structure. Fig. 1 shows a characteristic part of the structure along a threefold axis. Table 3 lists bond distances and angles. The structure is essentially the same as that of Grund & Preisinger (1950) but with all atoms except those of the H_2O molecules shifted by an average of 0.10 \AA ; the O atoms of the H_2O molecules are shifted by an average of 0.56 \AA .

The SbS_4 tetrahedron with pentavalent Sb has point symmetry 3. The two independent Sb—S bonds are almost equal in length and average 2.33 \AA . Similar average distances (Sb—S = $2.32-2.35 \text{ \AA}$) have been found for the SbS_4 tetrahedra in K_3SbS_4 , Na_3SbS_4 and $(\text{NH}_4)_3\text{SbS}_4$ (Graf & Schäfer, 1976). In all cases the

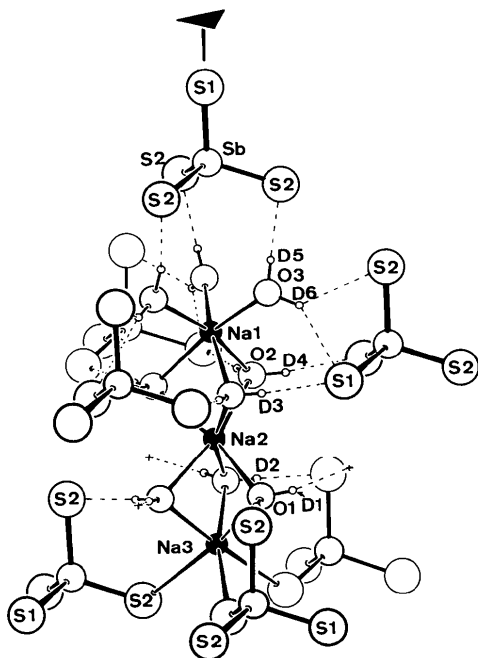


Fig. 1. Perspective view of the structure perpendicular to a threefold axis. + denotes an O(3) position.

Sb—S bonds are significantly shorter than those of isolated $\text{Sb}^{\text{III}}\text{S}_3$ pyramids, which have typical Sb—S distances of 2.45 \AA in tetrahedrite, $\text{Cu}_{12}(\text{SbS}_3)_4\text{S}$ (Wuensch, 1964), or 2.46 \AA in pyrargyrite, Ag_3SbS_3 (Engel & Nowacki, 1966).

The Na^+ ions are six-coordinated and form a finite group of three face-sharing coordination polyhedra, $\{[\text{H}_2\text{O}(3)]_3\text{Na}(1)[\text{H}_2\text{O}(2)]_3\text{Na}(2)[\text{H}_2\text{O}(1)]_3\text{Na}(3)-\text{S}(2)_3\}$, along the threefold axis. All three Na coordination figures may be described as strongly distorted octahedra with $\text{O}-\text{Na}-\text{O}$, S angles that deviate up to 26° from 90 and 180° . The torsion angles for each

Table 3. *Interatomic distances (Å) and angles (°)*

Distances and angles which were fixed during X-ray refinement are denoted by *.

	X-ray	Neutron	X-ray	Neutron
(a) Na^+ ions				
$\text{Na}(1)-\text{O}(3) \times 3$	2.359 (4)	2.358 (5)		
$-\text{O}(2) \times 3$	2.423 (4)	2.436 (5)		
Mean value	2.391	2.397		
			O—Na—O	
$\text{O}(3)-\text{O}(3) \times 3$	3.404 (5)	3.408 (5)	92.4 (1)	92.6 (1)
$-\text{O}(2) \times 3$	3.282 (5)	3.286 (5)	86.7	86.5
$-\text{O}(2) \times 3$	3.731 (5)	3.741 (5)	102.6	102.6
$-\text{O}(2) \times 3$			165.1	164.9
$\text{O}(2)-\text{O}(2) \times 3$	3.084 (5)	3.096 (5)	79.0	78.9
$\text{Na}(2)-\text{O}(2) \times 3$	2.417 (4)	2.425 (5)		
$-\text{O}(1) \times 3$	2.387 (4)	2.395 (5)		
Mean value	2.402	2.410		
			O—Na—O	
$\text{O}(2)-\text{O}(2) \times 3$	3.084 (5)	3.096 (5)	79.3 (1)	79.4 (1)
$-\text{O}(1) \times 3$	3.399 (5)	3.413 (5)	90.1	90.1
$\text{O}(1) \times 3$	4.075 (5)	4.091 (5)	116.1	116.1
$-\text{O}(1) \times 3$			159.6	159.5
$\text{O}(1)-\text{O}(1) \times 3$	3.034 (5)	3.039 (5)	78.9	78.7
$\text{Na}(3)-\text{O}(1) \times 3$	2.380 (4)	2.382 (5)		
$-\text{S}(2) \times 3$	2.996 (3)	2.998 (5)		
			O,S—Na—O,S	
$\text{O}(1)-\text{O}(1) \times 3$	3.034 (5)	3.039 (5)	79.2 (1)	79.3 (1)
$-\text{S}(2) \times 3$	3.779 (4)	3.774 (6)	88.6	88.3
$-\text{S}(2) \times 3$	4.300 (4)	4.292 (6)	105.7	105.3
$-\text{S}(2) \times 3$			165.8	165.8
$\text{S}(2)-\text{S}(2) \times 3$	4.160 (3)	4.180 (7)	87.9	88.4
(b) SbS_4 tetrahedron				
Sb—S(1)	2.326 (2)	2.331 (5)		
$-\text{S}(2) \times 3$	2.330 (2)	2.320 (5)		
Mean value	2.329	2.326		
			S—Sb—S	
$\text{S}(1)-\text{S}(2) \times 3$	3.777 (3)	3.778 (7)	108.4 (1)	108.7 (1)
$\text{S}(2)-\text{S}(2) \times 3$	3.828 (3)	3.808 (7)	110.5	110.3
(c) Coordination around S				
			Sb—S(1)—H,D	
$\text{S}(1)-\text{Sb}$	2.326 (2)	2.331 (5)		
$-\text{H}_i\text{D}(3) \times 3$	2.411 (6)	2.403 (7)	125.8	126.4 (1)
$-\text{H}_i\text{D}(6) \times 3$	2.811 (47)	2.830 (7)	74.8	75.6 (1)
			Sb—S(2)—Na/H,D	
$\text{S}(2)-\text{Sb}$	2.330 (2)	2.320 (5)		
$-\text{Na}(3)$	2.996 (3)	2.998 (5)	122.0	122.2 (2)
$-\text{H}_i\text{D}(1)$	2.391 (6)	2.379 (6)	94.3	94.9 (2)
$-\text{H}_i\text{D}(4)$	2.364 (11)	2.362 (6)	103.5	103.6 (2)
$-\text{H}_i\text{D}(5)$	2.359 (16)	2.338 (7)	100.5	102.2 (2)
$-\text{H}_i\text{D}(6)$	2.822 (47)	2.861 (8)	74.6	75.1 (2)

Table 3 (cont.)

(d) Coordination around O											
	X-ray	Neutron		X-ray	Neutron						
O(1)—Na(2)	2.387 (4)	2.395 (5)	Na(2)—O(1)—Na(3)	85.4	85.5 (1)						
—Na(3)	2.380 (4)	2.382 (5)	—H,D(1)	117.8	120.6 (3)						
—H,D(1)	0.96*	0.967 (4)	—H,D(2)	113.5	108.5 (3)						
—H,D(2)	0.96*	0.947 (4)	Na(3)—O(1)—H,D(1)	109.7	113.8 (3)						
			—H,D(2)	121.5	120.0 (3)						
O(2)—Na(1)	2.423 (4)	2.436 (5)	H,D(1)—O(1)—H,D(2)	108*	107.8 (4)						
—Na(2)	2.417 (4)	2.425 (5)	Na(1)—O(2)—Na(2)	85.3	85.3 (1)						
—H,D(3)	0.96*	0.959 (5)	—H,D(3)	104.9	106.8 (3)						
—H,D(4)	0.96*	0.961 (5)	—H,D(4)	124.7	123.3 (3)						
			Na(2)—O(2)—H,D(3)	108.9	109.2 (3)						
O(3)—Na(1)	2.359 (4)	2.358 (5)	—H,D(4)	122.5	123.5 (3)						
—H,D(2)	1.888 (20)	1.874 (5)	H,D(3)—O(2)—H,D(4)	108*	106.7 (4)						
—H,D(5)	0.96*	0.957 (5)	Na(1)—O(3)—H,D(2)	90.7	93.0 (2)						
—H,D(6)	0.96*	0.927 (6)	—H,D(5)	117.9	122.5 (4)						
			—H,D(6)	118.6	119.3 (4)						
			H,D(2)—O(3)—H,D(5)	112.3	106.8 (4)						
			—H,D(6)	107.8	105.2 (5)						
			H,D(5)—O(3)—H,D(6)	108*	106.8 (6)						

(e) Hydrogen bonds											
A	B	C	A—B	B—C	A—C	∠BAC	∠BAB'	∠CAC'	∠ABC		
O(1)—H(1)...	S(2)		0.96*	2.391 (6)	3.350 (4)	2	108*	118.7 (1)	177		
—D(1)...			0.967 (4)	2.379 (6)	3.343 (6)	3.3 (3)	107.8 (4)	119.0 (1)	175.4 (4)		
O(1)—H(2)...	O(3)		0.96*	1.888 (20)	2.808 (5)	13			160		
—D(2)...			0.947 (4)	1.874 (5)	2.807 (5)	8.2 (2)			167.7 (3)		
O(2)—H(3)...	S(1)		0.96*	2.411 (6)	3.369 (4)	3	108*	107.1 (1)	176		
—D(3)...			0.959 (5)	2.403 (7)	3.358 (6)	4.3 (3)	106.7 (4)	107.3 (1)	173.9 (4)		
O(2)—H(4)...	S(2)		0.96*	2.364 (11)	3.316 (4)	6			172		
—D(4)...			0.961 (5)	2.362 (6)	3.319 (6)	4.8 (3)			173.2 (4)		
O(3)—H(5)...	S(2)		0.96*	2.359 (16)	3.305 (4)	8	108*		168		
—D(5)...			0.957 (5)	2.338 (7)	3.293 (6)	2.9 (3)	106.8 (6)		175.9 (4)		
O(3)—H(6)...	S(1)		0.96*	2.811 (47)	3.584 (4)	31		134.4 (1)	138		
—D(6)...			0.927 (6)	2.830 (7)	3.588 (4)	30.6 (4)		134.8 (2)	139.8 (5)		
O(3)—H(6)...	S(2)			2.822 (47)	3.589 (4)	32		74.1 (1)	138		
—D(6)...				2.861 (8)	3.594 (6)	32.9 (4)		74.6 (1)	137.0 (5)		

octahedron, defined by ligand *A*—threefold axis of the Na octahedron—ligand *B*, are 45, −32 and 43° for Na(1), Na(2) and Na(3) respectively. The torsion angle for the Na(2) polyhedron is near the transition from an octahedron (ideal torsion angle = 60°) to a trigonal prism (ideal torsion angle = 0°). It appears that the torsion angles are strongly controlled by the spatial arrangement of the SbS₄ tetrahedra through the formation of approximately equidistant O—H...S bonds of the water molecules. The Na—O bonds of Schlippe's salt average 2.39 Å, which is close to the average Na—O distance of 2.44 Å given by Cocco, Fanfani & Zanazzi (1972) for NaO₆ octahedra. The Na(3)—S(2) bond, 3.00 Å, compares well with the average Na—S distance of 2.98 Å for the NaS₆ octahedra of Na₃AsS₃ (Palazzi, 1976).

Hydrogen bonding

Schlippe's salt exhibits an extensive hydrogen-bond system between the water molecules and the S atoms of the SbS₄ group. Fig. 2 shows the environment of the S atoms, Fig. 3 the coordination around the three symmetry-independent D₂O molecules. D₂O(1) and D₂O(2) are bonded to two Na ions and have approximately tetrahedral environments, while D₂O(3) is

bonded only to one Na⁺ ion. The O—D bonds and the D—O—D angles vary in the usual range. Four essentially linear O—D...S bonds, O...S = 3.30–3.36, D...S = 2.34–2.40 Å, and one O—D...O bond, also approximately linear, O...O = 2.81 Å, are observed. The D...S,O distances of these bonds are 0.4–0.5 Å shorter than the sum of the van der Waals radii (H, 1.0 Å, Baur, 1972; S, 1.8, O, 1.4 Å, Bondi, 1964) and fulfill therefore the operational criterion of Hamilton & Ibers (1968) for the detection of hydrogen bonding. D(6) of D₂O(3) does not fulfill this criterion. It has weak interactions with two S atoms, D(6)...S(1) = 2.82, D(6)...S(2) = 2.86 Å, while both corresponding O(3)...S distances are 3.59 Å. However, O—H and O—D stretching frequencies derived from Raman spectra of Schlippe's salt (Mikenda & Preisinger, 1978) indicate that all H and D atoms of the compound are involved in hydrogen bonding. Therefore the D(6)...S(1),S(2) interaction is interpreted as a weak, bifurcated hydrogen bond.

The D(6) temperature factors refined to strongly anisotropic values. The longest axis of the vibration ellipsoid with an r.m.s. amplitude of 0.5 Å is approximately normal to the O(3)—D(6) bond and approximately parallel to the D(5)—O(3)—D(6) plane; that is, also approximately parallel to the plane defined by the

D(6) donor, O(3), and by the two D(6) acceptors, S(1) and S(2). On the other hand, the vibration ellipsoids of D(5) and O(3) are smaller and do not exhibit a similar anisotropy. Least-squares refinements with the retention of a reasonable D₂O geometry (D—O—D angle close to 108°, as would be indicated by ¹H NMR measurements on Na₃SbS₄·9H₂O which give the usual

H—H distances of 1.59 Å) do not support a splitting of the D(6) position into two equal, half-occupied positions. Low-temperature measurements are in progress to determine whether there is a single or double minimum potential for D(6) (Mereiter, Preisinger, Guth, Mikenda & Hiebl, 1978).

Table 4 gives a comparison of salt hydrates with O—H...S and O—D...S bonds. Except for the bifurcated O—D...S bond of Schlippe's salt, the O—S distances range from 3.21–3.52 Å with an average of 3.32 Å. Only three of these compounds, including Schlippe's salt, have been investigated by neutron diffraction. The H,D...S distances of these three range from 2.34–2.41 Å.

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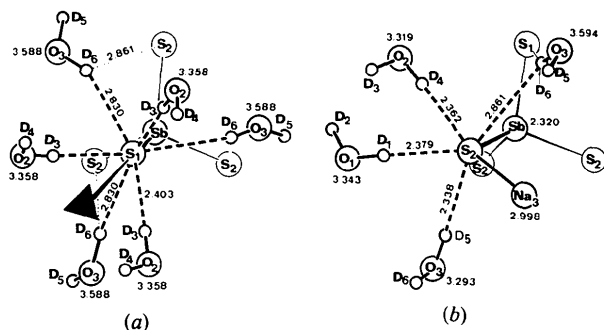


Fig. 2. Coordination of the S atoms: (a) for S(1) and (b) for S(2).

Table 4. Comparison of O—H(D)...S bond lengths (Å)

Compound	Diffraction method	O...S range	O...S average	O—H(D)	H(D)...S	Number of different bonds	References
Na ₃ SbS ₄ ·9D ₂ O	<i>N</i>	3.293–3.358 (3.588/3.594)	3.328	0.947–0.967 (0.927)	2.338–2.403 (2.830/2.861)	4 (1)* 4 (1)*	This work
Na ₃ SbS ₄ ·9H ₂ O	<i>X</i>	3.305–3.369 (3.584/3.589)	3.335				
BaS ₂ O ₃ ·H ₂ O	<i>N</i>	3.298	3.298	0.960	2.367	1†	
Na ₂ S ₂ O ₃ ·5H ₂ O	<i>N</i>	3.336–3.359	3.346	0.956–0.960	2.390–2.408	4	Lisensky & Levy (1978)
MgS ₂ O ₃ ·6H ₂ O	<i>X</i>	3.255–3.263	3.259			3	Baggio, Amzel & Becka (1969)
K ₂ SnS ₃ ·2H ₂ O	<i>X</i>	3.245–3.337	3.284			3	Schiwy, Blutau, Gähje & Krebs (1975)
Na ₄ SnS ₄ ·14H ₂ O	<i>X</i>	3.206–3.523	3.334			11	Schiwy, Pohl & Krebs (1973)
Na ₄ Sn ₂ S ₆ ·14H ₂ O	<i>X</i>	3.242–3.396	3.320			11	Krebs, Pohl & Schiwy (1972)
Na ₄ Ge ₂ S ₆ ·14H ₂ O	<i>X</i>	3.224–3.430	3.309			11	Krebs, Pohl & Schiwy (1972)
Na ₃ AsO ₂ S ₂ ·11H ₂ O	<i>X</i>	3.23–3.53	3.35			5	Jaulmes & Palazzi (1976)
Na ₂ S·5H ₂ O	<i>X</i>	3.27–3.45	3.34			3	Bedlivy & Preisinger (1965a)
Na ₂ S·9H ₂ O	<i>X</i>	3.24–3.49	3.34			6	Bedlivy & Preisinger (1965b)
Mean		3.21–3.52	3.324			66	

* Bifurcated bond, omitted from mean.

† H₂O molecule orientationally disordered.

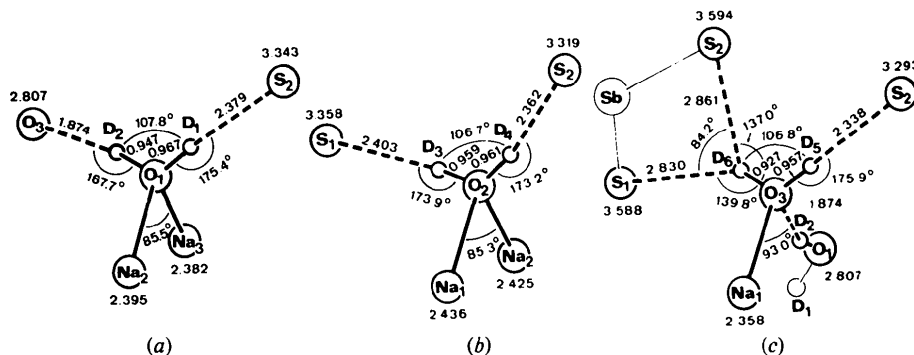


Fig. 3. Coordination of the D₂O molecules: (a) for D₂O(1), (b) for D₂O(2) and (c) for D₂O(3).

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Variation in $d(T-O)$, $d(T\cdots T)$ and $\angle TOT$ in Silica and Silicate Minerals, Phosphates and Aluminates

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Abstract

The interdependences between tetrahedral $d(T-O)$ bond lengths, nonbonded $d(T\cdots T)$ separations and TOT angles ($T = \text{Al, Si, P}$) are examined by regression analysis. The dependence between $d(T\cdots T)$ and $\angle TOT$ improves in the sequence P, Si and Al while the $d(T-O)$ on $\angle TOT$ dependence deteriorates. A continuous range of $d(\text{Si}\cdots\text{Si})$ values observed for silicates, siloxanes and silicides between bonded and proposed nonbonded separations suggests that a 'hard-

sphere' nonbonded radius for Si may not be realized in solids.

Introduction

In the last ten years there have been several studies devoted to understanding variations in Si—O bond length, $d(\text{Si—O})$, nonbonded Si \cdots Si separations, $d(\text{Si}\cdots\text{Si})$, and SiOSi angles, $\angle\text{SiOSi}$, in the silica polymorphs. However, the small variation in $d(\text{Si—O})$