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Hydrogen bonds in Schlippe's salt, $Na_3SbS_4 \cdot 9\,H_2O$ and $Na_3SbS_4 \cdot 9\,D_2O$: Diffraction and spectroscopic studies in the temperature range of 75 K to 295 K*

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Abstract. The work on the crystal structure of Schlippe's salt, done by X-ray and neutron diffraction studies at room temperature (Mereiter et al., 1979), has now been supplemented by the neutron diffraction study of $Na_3SbS_4 \cdot 9\,D_2O$ at 105 K and by Raman and ^{1}H-NMR spectroscopic investigations in the temperature range of 75–295 K. For $Na_3SbS_4 \cdot 9\,D_2O$ at 105 K, the space group is $P2_13$, $a = 11.878$ Å, $Z = 4$. Least-squares refinement of the neutron data converged to $R(F) = 0.043$ for 857 observed reflections. Compared with the structure at room temperature, there are minor changes in atomic coordinates; thermal vibrations are strongly reduced at 105 K. Observed bond lengths within the SbS_4 tetrahedron and the D_2O molecules are slightly larger at 105 K than at room temperature (bond lengths not corrected for thermal motion) while Na–O,S and hydrogen bonds decrease in length. Average bond lengths at 105 K are $Sb-S = 2.333$, $Na-O = 2.377$, $O-D = 0.963$ Å. ^{1}H-NMR spectra show the usual doublet pattern of water molecules with an average intramolecular H–H distance of 1.546 Å at 95 K. At low temperatures an additional intermolecular spin-spin coupling could be observed. Raman spectra of both the H and the D compounds of Schlippe's salt are well resolved at low temperatures. The observed O–H(D) stretching frequencies, $\bar{\nu}(O-H) = 3309-3422$, $\bar{\nu}(O-D) = 2448-2550\ \mathrm{cm}^{-1}$, show that all hydrogen bonds

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* Dedicated to Prof. W. Nowacki on occasion of his 70th birthday

of Schlippe's salt – one O – H(D) ... O, four approximately linear O – H(D) ... S, and one fairly symmetric bifurcated O – H(D) ... S,S bond – are nearly equal in strength.

Introduction

The structure of Schlippe's salt has been studied at room temperature for $Na_3SbS_4 \cdot 9H_2O$ with X-ray diffraction and for $Na_3SbS_4 \cdot 9D_2O$ with neutron diffraction (Mereiter et al., 1979). The present study further characterizes O – H ... S bonds in Schlippe's salt by a neutron diffraction investigation at 105 K and by ^{1}H-NMR and Raman spectroscopic measurements at different temperatures. The goal of this work is to obtain a better understanding of the nature of O – H ... S bonds and to clarify some questions posed by the room temperature diffraction studies.

Experimental

X-ray investigation

Crystal data are summarized in Table 1. Accurate lattice parameters for $Na_3SbS_4 \cdot 9H_2O$ and $Na_3SbS_4 \cdot 9D_2O$ have been determined by X-ray diffraction at 293 K and at 133 ± 5 K with a Philips PW1100 four-circle diffractometer using Ag$K\alpha$ radiation. From these values the lattice parameters at 105 K, the temperature of the neutron diffraction experiment, have been calculated. A linear temperature dependency, confirmed for the temperature range 133 – 293 K, was assumed.

Neutron diffraction and refinement

Intensity data were collected on the *P* 32 automatic four-circle diffractometer in the reactor FR2 at the Kernforschungszentrum Karlsruhe. A monochromatic neutron beam [$\lambda_N = 1.0237(5)$ Å] was obtained with a focusing Cu(311) crystal. The neutron flow at the sample was $3.6 \times 10^6\ s^{-1}\ cm^{-2}$ as determined by gold foil activation analysis. A sample temperature of 105 ± 5 K was maintained with a Displex Split-Cycle Refrigerator (Air Products & Chemicals, model CS-1003). Prior to data collection the nearly ideal $Na_3SbS_4 \cdot 9D_2O$ crystal of 25 mm^3 volume was treated with liquid nitrogen to minimize extinction effects. A mosaic spread with a half width of $\Delta M = 0.23(3)^\circ$ was calculated from peak profile analysis.

During intensity measurements the crystal was surrounded by a cooling device which also scattered the neutron beam, causing a background

Table 1. Crystallographic data

	$Na_3SbS_4 \cdot 9H_2O$	$Na_3SbS_4 \cdot 9D_2O$	Remarks
	Cubic, space group $P2_13$, $Z = 4$		
a at 293 K	11.959(1) Å	11.959(1) Å	[1] redetermined, this work
a at 293 K	11.957(2)	11.961(2)	[2] Haussühl (1970)
a at 133 ± 5 K	11.887(2)	11.890(2)	[3] this work
a at 105 K	11.875	11.878	[4] calculated from [1] and [3] assuming a linear temperature dependency
a at 105 K	11.870	11.883	[5] calculated from [2] and [6]
Linear thermal expansion coefficient α	38.8×10^{-6}	34.9×10^{-6}	[6] Haussühl (1970), determined for the temperature range 253–293 K by dilatometric measurements

dependent on the 2θ angle. Therefore an ω-scan with fixed counter was selected for data collection and the resulting constant background could be simply and reliably eliminated in the intensity calculations. Individual reflections were measured by a step scan with a variable ω-dependent scan width, but with a fixed number of steps and constant step time. Thus all reflections were measured with comparable accuracy. The orientation of the crystal on the diffractometer was determined from 14 reflections and also measured were 2082 intensities for which $(\sin\theta)/\lambda \leq 0.75$ Å^{-1}. After averaging equivalent reflections 1088 remained of which 857 were considered as observed $[I_{hkl} > 2 \times \sigma(I_{hkl})]$. The reliability factor for the symmetrically equivalent reflections was calculated by $R = \Sigma|\bar{I}_{hkl} - I_{hkl}|/\Sigma I_{hkl} = 0.030$.

The intensities I_{hkl} and the standard deviations $\sigma(I_{hkl})$ for the refinement were calculated as follows:

$$I_{hkl} = \mathrm{NORM} \times (I_{\mathrm{int}} - B_{\mathrm{av}} \times \mathrm{N} \times T_s/T_b) = \mathrm{NORM} \times I_{\mathrm{cor}}$$

$$\sigma(I_{hkl}) = \mathrm{NORM} \times (0.0004 \times I_{\mathrm{cor}}^2 + I_{\mathrm{int}} + 0.5\, B_{\mathrm{av}} \times \mathrm{N}_2 \times T_s^2/T_b^2)^{1/2}$$

where $\mathrm{NORM} = 100 \times \Delta\omega/T_s$

T_s = counting time for one ω step,
T_b = counting time for one background measurement,
I_{int} = integrated intensity from sum of steps,
B_{av} = average of the background measured left and right of peak,
N = the number of steps.

The structure was refined by full-matrix least-squares starting with the parameters of the room temperature structure and using scattering lengths from Willis (1973). The function $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$ was

Table 2. Atomic coordinates ($\times 10^5$) and B_{eq} [Å^2] for Schlippe's salt. Each first line: 105 K data for $Na_3SbS_4 \cdot 9\,D_2O$. Each second line: room temperature structure [Mereiter et al, 1979); atomic coordinates for Na, Sb, S, and O are weighted average values from X-ray and neutron data, all other values are from the neutron data

	x	y	z	B_{eq}
Na(1)	29175(24)	x	x	0.72
	29154(11)			2.38
Na(2)	44977(23)	x	x	0.66
	45002(11)			2.38
Na(3)	60484(24)	x	x	0.66
	60621(12)			2.64
Sb	03840(15)	x	x	0.52
	03723(2)			2.00
S(1)	92520(31)	x	x	0.79
	92488(8)			3.43
S(2)	15051(28)	15032(30)	92169(29)	0.58
	14838(8)	14807(8)	92203(8)	2.36
O(1)	−02558(15)	36670(15)	92586(15)	0.65
	−02650(19)	36677(16)	92593(16)	2.76
O(2)	18500(15)	69551(15)	99234(15)	0.74
	18415(19)	69540(17)	99270(16)	2.97
O(3)	10095(15)	25624(16)	33022(16)	0.82
	10098(18)	25605(19)	32864(21)	3.29
D(1)	02305(17)	30139(16)	92029(17)	1.73
	02163(29)	30189(25)	92121(28)	4.00
D(2)	−07450(16)	36616(17)	86074(16)	1.54
	−07326(28)	36684(26)	86187(27)	3.87
D(3)	25285(17)	66112(17)	02037(17)	1.81
	25114(32)	66185(31)	02221(31)	4.57
D(4)	16960(17)	75891(16)	04109(17)	1.75
	16799(29)	75864(27)	03976(27)	4.18
D(5)	04849(18)	22898(19)	27438(19)	2.17
	05069(31)	22681(37)	27323(36)	5.12
D(6)	05965(21)	30799(18)	37455(23)	2.84
	06031(48)	30690(34)	37063(56)	7.47

minimized. Because of their low values, temperature factors for all atoms occupying the threefold axis could be refined isotropically. All other atoms were refined with anisotropic temperature factors. An isotropic extinction correction (Larson, 1970) was also applied. The largest correction factor was 0.94. The final $R(F) = 0.043$ and $Rw(F) = 0.031$ for 857 observed re-

Table 3. Atomic thermal parameters ($\times 10^4$). T.F. $= \exp\,[-2\pi^2\,(U_{11}a^{*2}h^2 + \ldots + 2\,U_{23}b^*c^*kl)]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na(1)	91(9)	U_{11}	U_{11}	–	–	–
Na(2)	83(9)	U_{11}	U_{11}	–	–	–
Na(3)	84(8)	U_{11}	U_{11}	–	–	–
Sb	66(5)	U_{11}	U_{11}	–	–	–
S(1)	100(11)	U_{11}	U_{11}	–	–	–
S(2)	42(14)	101(15)	78(14)	9(12)	15(12)	4(12)
O(1)	97(7)	70(7)	81(7)	9(6)	11(7)	−10(6)
O(2)	91(7)	95(7)	95(8)	−11(7)	0(6)	−26(7)
O(3)	83(8)	93(8)	137(8)	12(6)	7(7)	6(7)
D(1)	242(9)	170(8)	247(9)	73(8)	10(8)	−36(7)
D(2)	208(8)	216(9)	160(8)	−3(7)	−55(7)	−18(7)
D(3)	185(9)	247(9)	255(9)	33(8)	−55(8)	−5(8)
D(4)	259(9)	192(9)	213(9)	9(8)	1(8)	−57(8)
D(5)	227(10)	306(11)	292(11)	−43(9)	−81(8)	50(9)
D(6)	363(12)	207(10)	509(15)	55(10)	206(11)	−61(11)

flections. Computer programs of the X-ray system (Stewart, 1976) were used.

Final atomic coordinates are given in Table 2. For comparison, the weighted average values of the room temperature X-ray and neutron structure determinations are also given in the same table. In Table 3 thermal parameters are listed.

^{1}H-NMR and Raman spectra

Broad line ^{1}H-NMR spectra were measured on a Bruker B-KR 22s spectrometer with a resonance frequency of 27 MHz. A Bruker Oscicomp was used for lowering the signal-to-noise ratio. The samples were powdered, sealed in a test tube, and exposed to a hard X-ray source to improve spin-lattice relaxation. Spectra were measured at four different temperatures between 295 K and 95 K.

Polarized and unpolarized Raman spectra of $Na_3SbS_4 \cdot 9\,H_2O$ and $Na_3SbS_4 \cdot 9\,D_2O$ single crystals were measured in the temperature range from 295 K down to 75 K. Standard Raman equipment with a Kr ion laser, double grating monochromator, and a liquid nitrogen cryostat with automatic temperature control was used. A more detailed description of Raman measurements and interpretation is given elsewhere (Mikenda and Preisinger, 1979).

Discussion

The structure of Schlippe's salt consists of groups of face-sharing Na coordination octahedra $\{[H_2O(3)]_3\ Na(1)\ [H_2O(2)]_3\ Na(2)\ [H_2O(1)]_3\ Na(3)\ S(2)_3\}$ (point symmetry 3) which share corners with SbS_4 tetrahedra (point symmetry 3) to form a framework structure. Six different hydrogen bonds, one O – H ... O and five O – H ... S bonds, contribute considerably to the stability of the structure. For a more detailed description of the structure the reader is referred to the room temperature structure determination (Mereiter et al., 1979).

Comparison of the structures at room temperature and at 105 K

The structures at room temperature (henceforth abbreviated by r.t.) and at 105 K are almost identical. Minor changes in bond lengths and bond angles have occurred (Table 4). The observed changes in detail are:

The lattice parameter a decreases by 0.081 Å from 11.959(1)Å at r.t. to 11.878 Å at 105 K. For the deuterate the linear thermal expansion coefficient α, when calculated from the X-ray data, is 36.1×10^{-6}. This is in good agreement with the 34.9×10^{-6} determined by Haussühl (1970). Values for the hydrate were also in good agreement (Table 1). These values are all in the usual range for highly hydrated salts.

The changes in fractional coordinates are slight, but in most cases statistically significant. All are less than 0.004, corresponding to shifts of 0.049 Å or less if the same lattice constant for the structures at r.t. and at 105 K is assumed.

Bond lengths change in a systematic way. Strong bonds, Sb—S and O – D, tend to be shorter at higher temperature (averaging 0.005 Å and 0.008 Å, respectively). This shift is also observed for other structures determined under similar temperature conditions. The explanation is that the ellipsoidal model of thermal vibration does not adequately describe the thermal motions of relatively rigid groups such as SbS_4 and D_2O. As a consequence, the apparent bond lengths within these groups decrease with increasing temperature.

On the contrary, the weak bonds, Na – O,S and the hydrogen bonds, decrease in length by an average of 0.028 Å at low temperature. The overall effect of increasing and decreasing bond lengths explains the change in the lattice parameter *a*.

Thermal vibrations are strongly reduced at 105 K and the r.m.s. amplitudes of Na, Sb, S, and O are almost exactly one-half of the r.t. values. For the deuterium atoms this reduction is smaller and amounts to $\approx 1/1.57$. Because of high and strongly anisotropic temperature factors at r.t., a splitting of the D(5) and D(6) positions and consequently a moderate orientational disorder of the $D_2O(3)$ molecule – to which both D's belong –

Table 4. Interatomic distances (Å) and angles (°) in Schlippe's salt. The room temperature values (r.t.) were calculated from the fractional coordinates given in Table 2. All values uncorrected for thermal motion effects

		105 K	r.t.	105 K	r.t.
(a) Na ions					
Na(1) – O(3)	× 3	2.350(2)	2.360(3)		
– O(2)	× 3	2.403(2)	2.428(3)		
Mean value		2.377	2.394	O – Na – O angle	
O(3) – O(3)	× 3	3.405(3)	3.407(4)	92.8(1)	92.4(1)
– O(2)	× 3	3.241(3)	3.285(4)	86.0	86.6
– O(2)	× 3	3.707(3)	3.737(4)	102.5	102.6
– O(2)	× 3			164.7	165.0
O(2) – O(2)	× 3	3.071(3)	3.091(4)	79.4	79.0
Na(2) – O(2)	× 3	2.407(2)	2.421(3)		
– O(1)	× 3	2.376(2)	2.392(3)		
Mean value		2.392	2.407	O – Na – O angle	
O(2) – O(2)	× 3	3.071(3)	3.091(4)	79.3(1)	79.3(1)
– O(1)	× 3	3.381(3)	3.406(4)	90.0	90.1
– O(1)	× 3	4.066(3)	4.083(4)	116.4	116.1
– O(1)	× 3			159.2	159.6
O(1) – O(1)	× 3	3.018(3)	3.037(4)	78.9	78.8
Na(3) – O(1)	× 3	2.350(2)	2.379(3)		
– S(2)	× 3	2.972(4)	2.996(3)	O – Na – O,S angle	
O(1) – O(1)	× 3	3.018(3)	3.037(4)	79.9(1)	79.3(1)
– S(2)	× 3	3.754(4)	3.776(3)	88.9	88.5
– S(2)	× 3	4.257(4)	4.296(3)	105.6	105.5
– S(2)	× 3			166.6	165.9
S(2) – S(2)	× 3	4.087(6)	4.164(3)	86.9	88.0

Table 4. (Continued)

		105 K	r.t.	105 K	r.t.	105 K	r.t.
(b) SbS_4 tetrahedron							
Sb–S(1)		2.329(7)	2.327(2)				
–S(2)	× 3	2.337(4)	2.329(2)				
Mean value		2.333	2.329	S–Sb–S angle			
S(1)–S(2)	× 3	3.783(5)	3.777(3)	108.4(1)	108.5(1)		
S(2)–S(2)	× 3	3.842(6)	3.826(3)	110.6	110.5		
(c) Coordination around S							
				Sb–S–D,Na angle			
S(1)–Sb		2.329(7)	2.327(2)				
–D(3)	× 3	2.379(4)	2.407(7)	126.1(1)	126.5(1)		
–D(6)	× 3	2.762(3)	2.829(7)	75.9(1)	75.7(1)		
S(2)–Sb		2.337(4)	2.329(2)				
–Na(3)		2.972(4)	2.996(3)	121.1(1)	122.1(1)		
–D(1)		2.348(4)	2.384(6)	94.1(1)	94.5(2)		
–D(4)		2.341(4)	2.358(6)	103.2(1)	103.5(2)		
–D(5)		2.304(4)	2.343(7)	101.9(1)	101.8(2)		
–D(6)		2.852(4)	2.856(8)	74.0(1)	75.1(2)		
(d) Coordination around O							
O(1)–Na(2)		2.376(2)	2.392(3)	Na(2)–O(1)–Na(3)		84.9(1)	85.4(1)
–Na(3)		2.350(2)	2.379(3)	–D(1)		121.1(2)	120.9(3)
–D(1)		0.969(3)	0.968(4)	–D(2)		109.2(2)	108.8(3)
–D(2)		0.967(3)	0.948(4)	Na(3)–O(1)–D(1)		114.6(2)	113.6(3)
				–D(2)		118.9(2)	119.7(3)
				D(1)–O(1)–D(2)		107.3(2)	107.7(4)

O(2) – Na(1)	2.403(2)	2.428(3)	Na(1) – O(2) – Na(2)	85.0(1)	85.2(1)
– Na(2)	2.407(2)	2.421(3)	– D(3)	105.9(2)	106.9(3)
– D(3)	0.963(3)	0.963(5)	– D(4)	124.5(2)	123.6(3)
– D(4)	0.967(3)	0.962(5)	Na(2) – O(2) – D(3)	109.0(2)	109.2(3)
			– D(4)	123.9(2)	123.7(3)
			D(3) – O(2) – D(4)	106.4(2)	106.3(5)
O(3) – Na(1)	2.350(2)	2.360(3)	Na(1) – O(3) – D(2)	92.9(1)	93.1(2)
– D(2)	1.834(3)	1.874(4)	– D(5)	123.3(2)	122.7(3)
– D(5)	0.966(3)	0.961(5)	– D(6)	119.4(2)	119.4(4)
– D(6)	0.946(3)	0.927(6)	D(2) – O(3) – D(5)	107.9(2)	106.6(4)
			– D(6)	105.0(2)	105.2(5)
			D(5) – O(3) – D(6)	105.4(3)	106.5(6)

(e) Hydrogen bonds (105 K values are listed above the room temperature values)

A B C	A – B	B – C	A – C	∢ BAC	∢ BAB′	∢ CAC′	∢ ABC
O(1) – D(1) . . . S(2)	0.969(3)	2.348(4)	3.314(4)	3.9(2)	107.3(2)	118.9(1)	174.5
	0.968(4)	2.384(5)	3.349(4)	3.3(3)	107.7(4)	118.8(1)	175.4
O(1) – D(2) . . . O(3)	0.967(3)	1.834(3)	2.786(3)	8.4(2)			167.1
	0.948(4)	1.874(5)	2.808(4)	8.2(2)			167.7
O(2) – D(3) . . . S(1)	0.963(3)	2.379(3)	3.340(3)	3.2(1)	106.4(2)	106.8(1)	175.5
	0.963(5)	2.407(5)	3.366(4)	4.5(3)	106.3(5)	107.2(1)	173.7
O(2) – D(4) . . . S(2)	0.967(3)	2.341(4)	3.304(4)	4.5(2)			173.6
	0.962(5)	2.358(5)	3.316(4)	4.6(3)			173.5
O(3) – D(5) . . . S(2)	0.966(3)	2.304(4)	3.268(4)	3.4(2)	105.4(3)		175.2
	0.961(5)	2.343(6)	3.302(4)	2.8(3)	106.5(6)		176.0
O(3) – D(6) . . . S(1)	0.946(3)	2.762(3)	3.545(3)	29.6(2)		134.1(1)	140.6
	0.927(7)	2.829(7)	3.586(4)	30.6(4)		134.4(1)	139.7
O(3) – D(6) . . . S(2)		2.852(4)	3.581(4)	34.5(2)		73.1(1)	134.7
		2.856(7)	3.590(4)	32.9(4)		74.1(1)	137.0

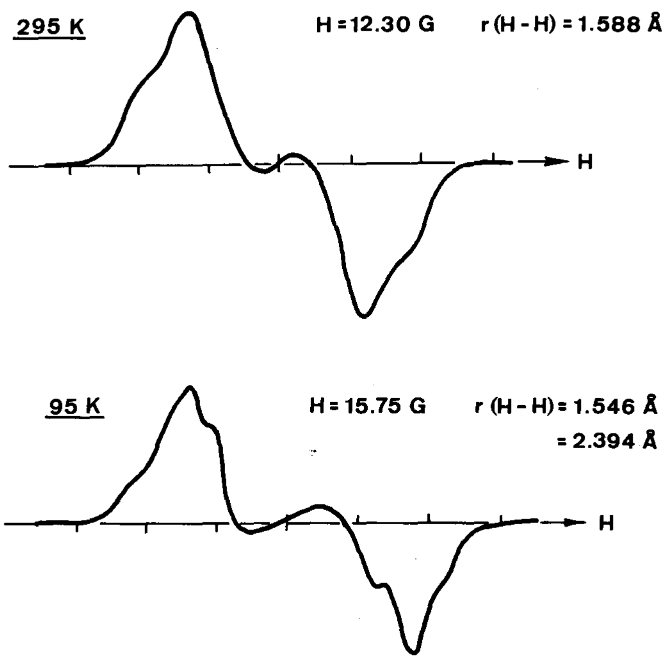

Fig. 1. Broad line ^{1}H-NMR spectra of $Na_3SbS_4 \cdot 9\,H_2O$

had been suggested (Mereiter et al., 1979). However at 105 K the thermal vibration parameters are strongly reduced (maximum r.m.s. amplitude 0.26 Å), and a splitting of D(5) and D(6) positions could be rejected by careful visual inspection of the Fourier peaks. Therefore an orientational disorder of the $D_2O(3)$ molecule can be excluded. Vibrational spectra support this view.

^{1}*H-NMR spectra*

The spectrum (Fig. 1) shows the familiar doublet pattern of a two spin system (Gutowsky et al., 1949), known from many hydrates. There is no significant change in the spectra down to 200 K. Only a small increase in line width, ΔH, and second moment, $\overline{\Delta H^2}$, are observed. This temperature effect is greatly enhanced when going down to 95 K (Table 5). H–H distances were calculated from second moments (Lösche, 1957). R(H–H) = 1.546 ± 0.003 Å at 90 K is an average value for the hydrogen pairs of the three different water molecules. The corresponding average distance from neutron data at 105 K, R(D–D) = 1.549 Å, is in satisfying agreement.

Table 5. Proton resonance data

Temperature	Line width	Second moment	Spin-spin distance
[K]	ΔH [G]	$\overline{\Delta H^2}$ [G^2]	R(H – H) [Å]
295	12.3	22.25(5)	1.588(3)
240	12.5	22.54(20)	1.585(3)
200	12.5	23.10(20)	1.579(3)
95	15.75	26.20(30)	1.546(3)
		1.90(20)	2.394(50)

Distances from neutron diffraction at 105 K:

Intramolecular... D(1) – D(2) = 1.560, D(3) – D(4) = 1.545, D(5) – D(6) = 1.542 Å;
Intermolecular... D(1) – D(4) = 2.484, D(2) – D(5) = 2.321, D(2) – D(6) = 2.271 Å,
further D – D distances are larger than 2.84 Å

Beside the usual H_2O doublet an additional line is observed in the 95 K spectrum indicating an intermolecular long-range coupling with R(H – H) = 2.39 ± 0.05 Å. From neutron data there are only three intermolecular D–D distances below 2.84 Å: D(2)–D(6) = 2.27, D(2)–D(5) = 2.32, and D(1) – D(4) = 2.48 Å. The long-range interaction observed in the 95 K spectrum is probably due to the H(2) – H(5) – H(6) triangle (Fig. 3c), but the low accuracy of broad line NMR in this distance range does not allow a more exact interpretation. The fact that long-range coupling cannot be observed at r.t. may be a consequence of considerably larger vibrational amplitudes of the hydrogen atoms, especially H(6).

Raman spectra

Since vibrational spectra are so sensitive to structural changes, they are particularly suitable for obtaining a quick survey spectrum of possible changes at low temperature. In the case of Schlippe's salt Raman spectra have certain advantages. Because of the factor group 23 (= *T*) all optical modes are Raman active, while in the IR spectrum only the polar *F*-modes are active.

A comparison of high and low temperature spectra (Mikenda and Preisinger, 1979) shows the usual differences due to temperature changes, but no indication of structural changes. There is a reasonable increase in the Raman frequencies and a considerable reduction in line widths when going from 295 K to 75 K. Thus many weaker and overlapping lines could be better identified. This is especially true for the majority of the H_2O (D_2O) librations and the translational modes. Figure 2 illustrates two examples. Considering isotope shifts, nine H_2O (D_2O) librations could be assigned with certainty in the low temperature spectra, exactly the number predicted from the crystal structure.

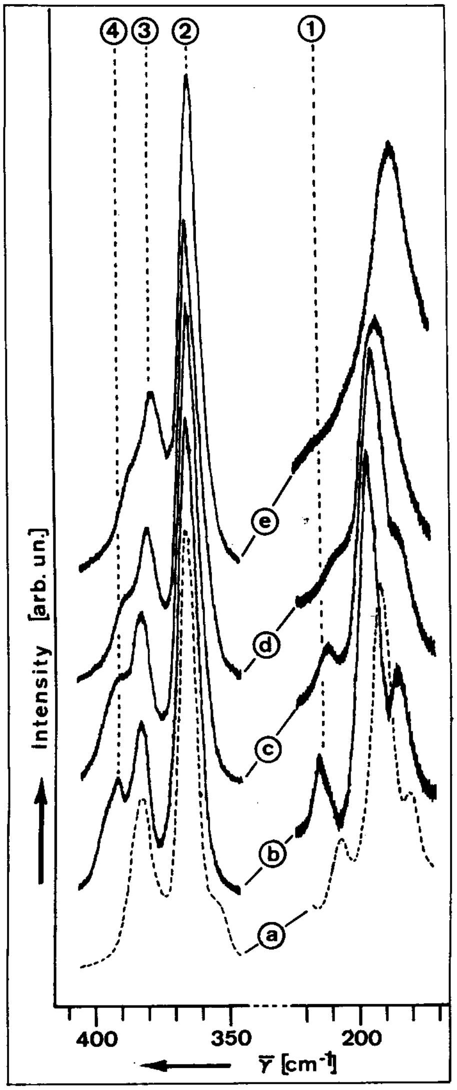

Fig. 2. Raman spectra (unpolarized) of Schlippe's salt.
(*a*) $Na_3SbS_4 \cdot 9D_2O$ at 75 K;
(*b*) $Na_3SbS_4 \cdot 9H_2O$ at 75 K;
(*c*) $Na_3SbS_4 \cdot 9H_2O$ at 120 K;
(*d*) $Na_3SbS_4 \cdot 9H_2O$ at 195 K;
(*e*) $Na_3SbS_4 \cdot 9H_2O$ at 295 K.
(*1*) Translational mode;
(*2*) SbS_4 symmetric stretch;
(*3*) SbS_4 asymmetric stretch;
(*4*) H_2O libration (corresponding D_2O libration at 283 cm^{-1})

It should be mentioned that spectra at 295 K and 75 K differ more than otherwise in one region, $\bar{\nu} = 170-200\,\mathrm{cm}^{-1}$ (Fig. 2). A series of Raman measurements made at 15 K increments showed that this difference was due to a particularly large frequency shift (about 10 cm^{-1}), but not to the appearance of a new line, which had seemed at least possible. Within the error limits the series gave no indication of a discontinuity or a temperature range where this shift might preferentially appear.

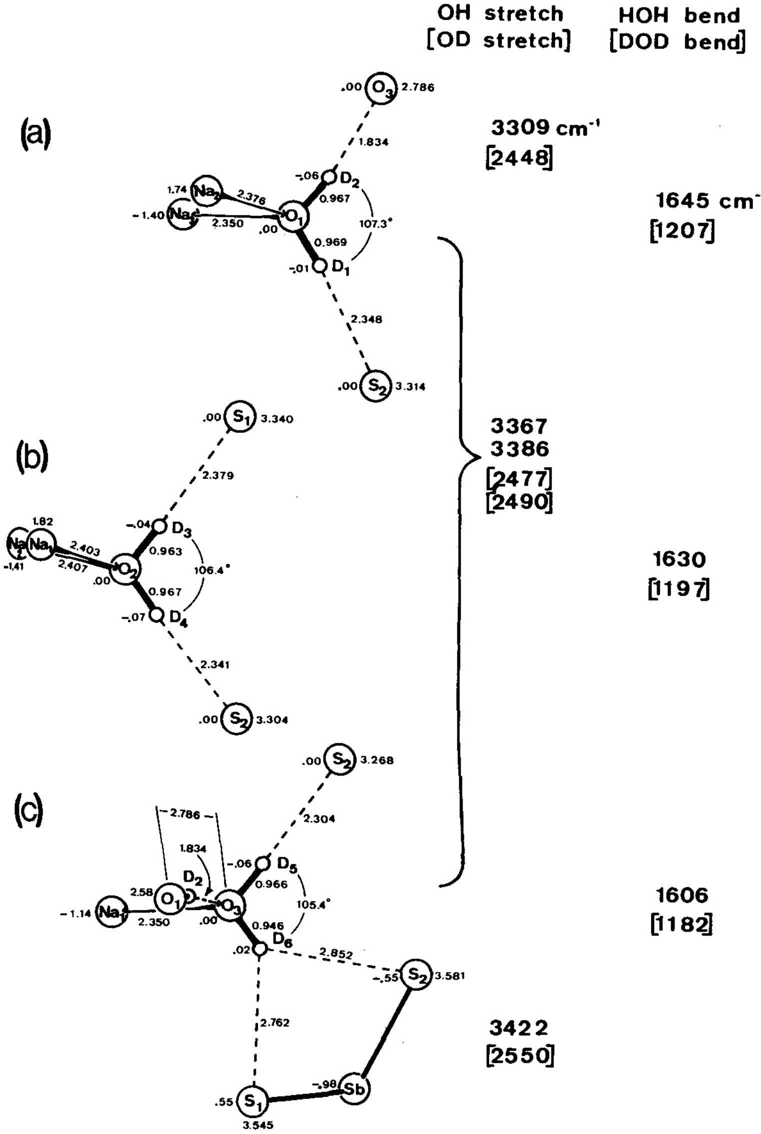

Fig. 3. Hydrogen bonds in Schlippe's salt at 105 K: (a), (b) and (c) denote the three different D_2O molecules of the structure. Numbers with two decimal places give heights (Å) above the plane of projection, numbers with three decimal places are bond lengths (Å). Assignment of Raman frequencies [cm^{-1}] for O – H (O – D) stretching and for H – O – H (D – O – D) bending frequencies to different O – H(D) ... Y bonds is based on H(D) ... Y distances

In the low temperature spectra four lines corresponding to O – H (O – D) stretching and three lines corresponding to H – O – H (D – O – D) bending frequencies could be identified. An estimate of the hydrogen bond strengths of the six different O – H groups, based on interatomic distances, results in the interpretation shown in Fig. 3. The values of the valence frequencies show definitely that all H(D) atoms are involved in hydrogen bonds of comparable strength.

In the case of the O – H(D)... O bond and the four approximately linear O – H(D)... S bonds, the H(D)... Y distances are distinctly less than the sum of the van der Waals radii (H: 1.0 Å, Bauer, 1972; S: 1.8, O: 1.4 Å, Bondi, 1964) which can be taken as a criterion for hydrogen bonding (Table 4e). This criterion does not apply to the bifurcated O – H,D(6) ... S(1),S(2) bond. In this case the H(D) ... S distances are nearly equal to the sum of the van der Waals radii. However the stretching frequencies ($\bar{\nu}_H < 3430\,\mathrm{cm}^{-1}$, $\bar{\nu}_D < 2560\,\mathrm{cm}^{-1}$) indicate that a considerable hydrogen bonding effect must be present. This bifurcated hydrogen bond is above all noteworthy for its almost perfect symmetry (Fig. 3c, Table 4e). Such nearly symmetric bifurcated hydrogen bonds are rare. Violuric acid is another example (Craven and Takei, 1964).

Summary

Through the combined application of diffraction and spectroscopic methods, through the measurements over a wide temperature range, and through the use of both the hydrate and the deuterate, a comprehensive and consistent view of the structure chemistry of Schlippe's salt could be obtained. The low temperature measurements made possible not only an improved determination of atomic positions, vibrational frequencies, and spin-spin interactions, but also established the absence of possible phase transformations. Disorder in the orientation of the $D_2O(3)$ molecule was found to be definitely nonexistent. It is noteworthy that there is a marked hydrogen bond system in which all O – H...Y bonds (Y = O or S or S,S participate to a comparative degree. Especially striking is that this applies to the nearly symmetrically branched bifurcated O – H(D)... S,S bond. Although H(D)... S distances in this bond are relatively large, from spectroscopic data one must conclude the existence of a considerable hydrogen bonding effect here, which would not be expected from structural data alone. The extent to which this can be observed for other sulfur acceptor systems should become apparent in future investigations.

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