

Crystal Structure of $\text{K}_3\text{SbS}_4 \cdot 4 \frac{1}{2} \text{H}_2\text{O}$

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Summary. The crystal structure of $\text{K}_3\text{SbS}_4 \cdot 4 \frac{1}{2} \text{H}_2\text{O}$, monoclinic, $P2_1/c-C_{2h}^5$, $a=12.732(3)$, $b=7.720(2)$, $c=13.928(4)$ Å, $\beta=90.19(1)^\circ$, $V=1369.0(5)$ Å³, $Z=4$, has been determined from X-ray single crystal data and refined by least-squares methods to $R=0.031$ for 3024 reflections. The structure is built up from $\text{KS}_{4-5}(\text{H}_2\text{O})_{3-5}$ polyhedra and SbS_4 tetrahedra ($\text{Sb-S}=2.327$ Å) which are three-dimensionally linked. The water molecules are bonded to two or three K^+ ions and form exclusively O-H...S-type hydrogen bonds. One of the five crystallographically different water molecule sites is due to space limitations only half occupied.

Keywords. Potassium tetrathioantimonate 4 ½-hydrate; Crystal structure; Hydrogen bond.

Die Kristallstruktur von $\text{K}_3\text{SbS}_4 \cdot 4 \frac{1}{2} \text{H}_2\text{O}$

Zusammenfassung. Die Kristallstruktur von $\text{K}_3\text{SbS}_4 \cdot 4 \frac{1}{2} \text{H}_2\text{O}$, monoklin, $P2_1/c-C_{2h}^5$, $a=12.732(3)$, $b=7.720(2)$, $c=13.928(4)$ Å, $\beta=90.19(1)^\circ$, $V=1369.0(5)$ Å³, $Z=4$, wurde mit Röntgen-Einkristalldaten bestimmt und für 3024 Reflexe auf $R=0.031$ verfeinert. Die Kristallstruktur ist aus dreidimensional verknüpften $\text{KS}_{4-5}(\text{H}_2\text{O})_{3-5}$ -Polyedern und SbS_4 -Tetraedern ($\text{Sb-S}=2.327$ Å) aufgebaut. Die Wassermoleküle sind an zwei bis drei Kaliumionen gebunden und bilden ausschließlich Wasserstoffbrücken des Typs O-H...S aus. Eine der fünf kristallographisch verschiedenen H_2O -Lagen ist aus Platzmangel nur zur Hälfte besetzt.

Introduction

Crystal structures with hydrogen bonds between water molecules as donor and sulfur as acceptor, like $\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$ [1], $\text{Na}_3\text{SbS}_4 \cdot 9 \text{H}_2\text{O}$ [2] or $\text{NaSCN} \cdot 2 \text{H}_2\text{O}$ [3], are a field of research work of our institute. A review on structural and vibrational spectroscopic aspects of these kind of hydrogen bonds has been given [4]. K_3SbS_4 is known to form a crystalline anhydrous compound [5] and the hydrated salt $\text{K}_3\text{SbS}_4 \cdot 4 \frac{1}{2} \text{H}_2\text{O}$ [6, 7]. Three other hydrates $\text{K}_3\text{SbS}_4 \cdot n \text{H}_2\text{O}$ with $n=3, 5$, and 6 were postulated from solubility studies [8], but lack by now any other experimental confirmation.

Experimental Part

The title compound was prepared by dissolving Sb_2S_5 (0.1 mol) in a solution of K_2S (0.3 mol) in 50 ml H_2O at $T=95^\circ\text{C}$. After filtration and evaporation (at room temperature in vacuum) of most of the water, the remaining oily orange liquid was allowed to crystallize in a refrigerator. Deliquescent

Table 1. Atomic parameters for $K_3SbS_4 \cdot 4 \frac{1}{2} H_2O$

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K(1)	0.07555(7)	0.56201(12)	0.39607(6)	370(4)	388(4)	342(4)	-28(4)	71(3)	-1(4)
K(2)	0.18634(9)	0.07489(13)	0.31064(7)	709(7)	393(5)	387(5)	-11(5)	58(5)	33(4)
K(3)	0.49671(9)	0.87404(16)	0.17778(10)	459(6)	612(7)	946(9)	-13(5)	106(6)	264(7)
Sb	0.24232(2)	0.50160(3)	0.14761(1)	253(1)	225(1)	215(1)	10(1)	26(1)	-14(1)
S(1)	0.29895(8)	0.67529(13)	0.27358(7)	411(5)	325(5)	302(4)	-57(4)	15(4)	-89(4)
S(2)	0.34496(8)	0.25163(13)	0.13852(7)	349(5)	287(4)	383(5)	81(4)	31(4)	-24(4)
S(3)	0.07091(7)	0.41217(13)	0.17838(7)	265(4)	368(5)	344(4)	-30(4)	35(3)	-38(4)
S(4)	0.25233(9)	0.65207(13)	0.00373(7)	508(6)	358(5)	286(4)	91(5)	90(4)	76(4)
O(1)	0.1375(3)	0.5093(4)	0.6046(3)	421(16)	314(15)	634(20)	-15(13)	-2(14)	62(15)
O(2)	0.0397(3)	0.2251(4)	0.4533(3)	513(19)	377(16)	466(17)	-79(14)	-122(14)	45(13)
O(3)	0.2838(3)	0.3388(5)	0.4093(3)	749(24)	620(23)	435(18)	-123(21)	-45(17)	87(17)
O(4)	0.5451(3)	0.5328(4)	0.1206(3)	485(20)	672(25)	758(25)	-42(17)	110(18)	-133(19)
O(5)	0.4611(3)	0.8957(4)	-0.0075(3)	510(35)	492(38)	511(37)	49(31)	70(28)	4(30)
H(1)	0.1852	0.4131	0.6031						
H(2)	0.1745	0.6102	0.5829						
H(3)	-0.0054	0.1366	0.4277						
H(4)	0.0647	0.1869	0.5148						
H(5)	0.2986	0.4538	0.3869						
H(6)	0.3046	0.3320	0.4755						
H(7)	0.4891	0.4529	0.1071						
H(8)	0.6005	0.5115	0.0756						
H(9)	0.5160	0.8405	-0.0434						
H(10)	0.4030	0.8169	-0.0040						

O(5), H(9) and H(10) are half-occupied (see text), H(9) and H(10) are in calculated positions. All other hydrogen atoms were refined as parts of rigid H_2O molecules with fixed O-H = 0.8 Å for X-ray scattering centres, O-H = 0.96 Å for nuclear H positions which are given here, and H-O-H = 108° for both. The e.s.d.'s of the rotation angles describing the H_2O orientations average 3.5°. A common isotropic temperature factor, $U_{iso} = 77(7) \text{ pm}^2$, was used for all H atoms. $ATF = \exp[-2\pi^2 (U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*)]$; U_{ij} given in pm^2

Table 2. Bond lengths (Å) and angles (°) with standard deviations in parentheses**a.** Coordination polyhedra of K

K(1) – S(1)	3.435(2)	K(2) – S(1)	3.441(2)	K(3) – S(1)	3.240(2)
– S(3)	3.246(2)	– S(2)	3.423(2)	– S(1)	3.553(2)
– S(3)	3.442(2)	– S(3)	3.509(2)	– S(2)	3.539(2)
– S(4)	3.488(2)	– S(3)	3.512(2)	– S(2)	3.387(2)
– O(1)	3.035(4)	– S(4)	3.316(2)	– O(3)	3.062(4)
– O(1)	2.767(4)	– O(1)	3.005(4)	– O(4)	2.821(4)
– O(2)	2.759(4)	– O(2)	2.967(4)	– O(4)	3.111(4)
– O(2)	3.045(4)	– O(3)	2.751(4)	– O(5)	2.624(4) or 3.013(4)
– O(3)	3.167(4)				(disorder, see text)

b. SbS_4 tetrahedron

Sb – S(1)	2.321(1)	S-Sb-S angles		
– S(2)	2.334(1)	110.2(1)		
– S(3)	2.330(1)	108.7(1)	106.9(1)	
– S(4)	2.320(1)	110.2(1)	109.6(1)	111.2(1)

c. Hydrogen Bonds. All water molecules were treated as rigid groups with O-H = 0.96 Å and H-O-H = 108° (see text); H-bonds marked with “*” are simultaneously edges of a K^+ coordination polyhedron

O	H	A	H-A	O-A	O-H-A
O(1) – H(1)	...	S(2)*	2.45(2)	3.354(4)	157(4)
O(1) – H(2)	...	S(4)*	2.36(1)	3.311(4)	170(5)
O(2) – H(3)	...	S(3)*	2.42(2)	3.341(4)	160(4)
O(2) – H(4)	...	S(3)*	2.40(2)	3.332(4)	162(4)
O(3) – H(5)	...	S(1)**	2.33(2)	3.219(4)	154(4)
O(3) – H(6)	...	S(2)	2.41(1)	3.357(4)	167(4)
O(4) – H(7)	...	S(2)*	2.45(2)	3.357(4)	158(4)
O(4) – H(8)	...	S(4)	2.52(2)	3.424(4)	157(4)
O(5) – H(9)	...	S(2)*	2.33	3.278(4)	171
O(5) – H(10)	...	S(4)	2.30	3.261(4)	174

yellowish crystals were obtained and stored in dry nitrogen atmosphere. A rounded fragment of about 0.3 mm diameter was selected in a glove box, mounted in a capillary and then transferred to a Philips PW1100 X-ray four-circle diffractometer equipped with Mo $K\alpha$ radiation and a graphite monochromator. Lattice parameters, determined by least-squares fit of 58 reflections with $8 < \Theta < 22^\circ$, were: $a = 12.732(3)$, $b = 7.720(2)$, $c = 13.928(4)$ Å, $\beta = 90.19(1)^\circ$, $V = 1369.0(5)$ Å³; $Z = 4$ $K_3SbS_4 \cdot 4 \frac{1}{2} H_2O$, mole weight 448.35, $D_x = 2.175$ g · cm⁻³, linear absorption coefficient $\mu(\text{Mo } K\alpha) = 35.1$ cm⁻¹. Laue symmetry and systematic extinctions were in accordance with the monoclinic space group $P2_1/c-C_{2h}^5$. Intensity data were collected at room temperature with ω -scans, scan width 1.2°, and a scan rate of 4° min⁻¹. Three standard reflections, monitored every 60 minutes, remained

constant within $\pm 2\%$. 4140 reflections with $2 < \Theta < 30^\circ$, $0 \leq h \leq 17$, $0 \leq k \leq 10$, $-19 \leq l \leq 19$ were measured, corrected for Lorentz-polarization and absorption effects (sphere, $\mu R = 0.5$), and averaged ($R_{int} = 0.030$) to 3989 unique reflections, 3024 of which with $F_o > 6\sigma(F_o)$ were subsequently used.

The structure was solved with direct methods and Fourier syntheses in space group $P2_1/c$. After a preliminary refinement ($wR = 0.041$) the H atoms of four water molecules were located from a weighted difference map, while those belonging to a fifth half-occupied H_2O site were assigned calculated positions. The final least-squares refinement minimized $\sum w(F_o - F_c)^2$ using a correction for extinction, neutral atom scattering functions with anomalous dispersion terms, anisotropic temperature factors for non-H atoms, one common isotropic temperature factor for H atoms, and rigid group constraints for H_2O molecules (O-H = 0.8 \AA for X-ray scattering centres, O-H = 0.96 \AA for nuclear H positions, and H-O-H = 108° for both; cf. Ref. [4]). Final residuals: $R = 0.031$, $wR = 0.035$ and $S = 1.44$ for 3024 reflections weighted by $w = 1/[\sigma^2(F_o) + 0.0002 \cdot F_o^2]$ and 129 refined parameters. All $\Delta/\sigma < 0.01$. The final difference map showed a largest peak of $1.6 e \cdot \text{\AA}^{-3}$, 0.8 \AA off from the potassium atom K(3). Calculations were carried out with programs SHELX76 [9] and PARST [10], drawings were prepared with ORTEP [11]. A list of structure factors is available from the authors.

Results and Discussion

Atomic parameters are given in Table 1, bond lengths and angles in Table 2, a view of the structure is shown in Fig. 1.

The structure determination showed the title compound to be indeed a $4 \frac{1}{2}$ -hydrate, and has thus confirmed the relatively old literature [6, 7]. Although the number and multiplicities of the crystallographic sites of the H_2O molecules would correspond to 5 H_2O per formula unit, the oxygen atom of the water molecule $H_2O(5)$ is located so close to a centre of inversion [0.9 \AA , hence $O(5)-O(5) = 2 \cdot 0.9 \text{ \AA}$] that it can at most be half occupied. The refinement of its occupation factor, which converged at $0.50(2)$, confirmed this consideration. Further geometric calculations showed that the cavity housing one pair of next neighboring $H_2O(5)$ positions, is slightly large for a single water molecule but by no means large enough to take up more than one molecule or $\frac{1}{2} H_2O$ per formula unit.

$K_3SbS_4 \cdot 4 \frac{1}{2} H_2O$ contains an almost regular SbS_4 tetrahedron with a mean bond length $\langle Sb-S \rangle = 2.327 \text{ \AA}$ and S-Sb-S angles ranging from 106.9 to 111.2° . The tetrahedron compares well with those in $Na_3SbS_4 \cdot 9 H_2O$, $\langle Sb-S \rangle = 2.329 \text{ \AA}$ [2], and three anhydrous alkali thioantimonates M_3SbS_4 , $\langle Sb-S \rangle = 2.33 \text{ \AA}$ [5]. In the

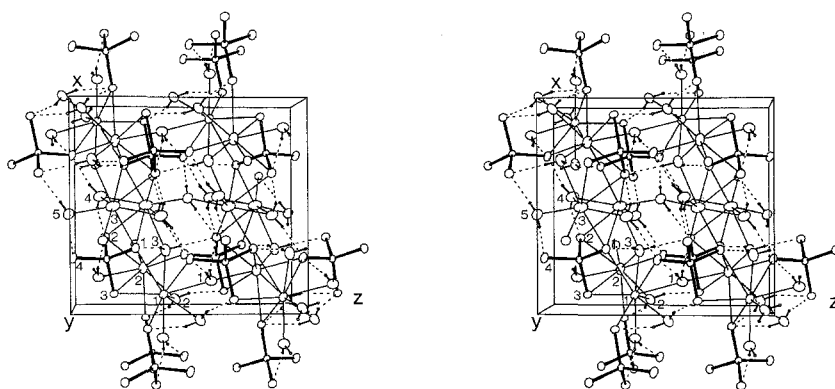


Fig. 1. Stereoview of the structure of $K_3SbS_4 \cdot 4 \frac{1}{2} H_2O$ along b

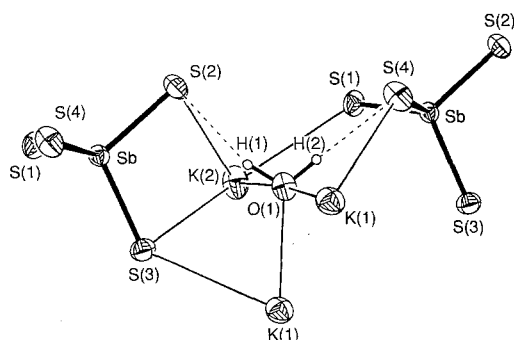


Fig. 2. Coordination of the water molecule $\text{H}_2\text{O}(1)$

title compound the SbS_4 tetrahedron is surrounded by 10 K^+ ions and linked to them via 13 K-S bonds (2, 3 or 4 K-S bonds per sulfur atom).

The K^+ ions display irregular coordination figures with coordination number 9 for the polyhedron $\text{K}(1)\text{S}_4(\text{H}_2\text{O})_5$ and 8 for the polyhedra $\text{K}(2)\text{S}_5(\text{H}_2\text{O})_3$ and $\text{K}(3)\text{S}_4(\text{H}_2\text{O})_4$. The water molecules are bonded either to three K^+ ions [O(1), O(2), O(3)] or to two K^+ ions [O(4), O(5)]. Table 2c shows that all molecules are involved in O-H...S bonds of the usual "straight" type, i.e. bonds to a single acceptor atom. O-H...O bonds or bifurcated O-H...S,S bonds, as found in $\text{Na}_3\text{SbS}_4 \cdot 9 \text{H}_2\text{O}$ [2] or $\text{Na}_3\text{AsS}_4 \cdot 8 \text{H}_2\text{O}$ [12], are lacking. O...S bond distances in $\text{K}_3\text{SbS}_4 \cdot 4 \frac{1}{2} \text{H}_2\text{O}$ range from 3.219 to 3.424 Å and average to 3.328 Å, close to the mean value $\langle \text{O} \cdots \text{S} \rangle = 3.326 \text{ \AA}$ of 75 straight O-H...S bonds reported in [4]. A typical example for the coordination of H_2O in $\text{K}_3\text{SbS}_4 \cdot 4 \frac{1}{2} \text{H}_2\text{O}$ is that of $\text{H}_2\text{O}(1)$ (Fig. 2), to which $\text{H}_2\text{O}(2)$ and $\text{H}_2\text{O}(3)$ resemble closely. It can be realized that $\text{H}_2\text{O}(1)$ is squeezed between three K^+ ions and that both O-H...S bonds of $\text{H}_2\text{O}(1)$ are simultaneously edges of the coordination polyhedra around two K^+ ions. This feature is hardly observed for hydrates with small cations (e. g. Na^+ , Mg^{2+}) and/or small anions as acceptors (O^{2-} , F^-) [13, 14] but seems to be more a rule rather than an exception if both H_2O -bonded cations and H-bond acceptors, here K^+ and S^{2-} , are large with respect to ionic radii. This conclusion is well supported by Table 2c where those seven out of ten O-H...S bonds which represent also edges of K^+ coordination polyhedra are marked by asterisks.

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