

- KEGGIN, J. F. (1934) *Proc. R. Soc. London Ser. A*, **144**, 75–100.
- KERR, S. & WILLIAMS, D. J. (1969). *Acta Cryst.* **B25**, 1183–1190.
- KIRFEL, S., WILL, G. & ARNDT, J. (1979). *Z. Kristallogr.* **149**, 315–326.
- KONNERT, J. H. & APPLEMAN, D. E. (1978). *Acta Cryst.* **B34**, 391–403.
- KONTA, J. & MRÁZ, L. (1961). *Am. Mineral.* **46**, 629–636.
- LEE, J. H. & GUGGENHEIM, S. (1981). *Am. Mineral.* **66**, 350–357.
- LENHART, P. G. (1975). *J. Appl. Cryst.* **8**, 568–570.
- LEVIEN, L., PREWITT, C. T. & WEIDNER, D. J. (1980). *Am. Mineral.* **65**, 920–930.
- LIEBAU, F. (1961). *Acta Cryst.* **14**, 1103–1109.
- LOUISNATHAN, S. J. & GIBBS, G. V. (1972) *Am. Mineral.* **57**, 1089–1108.
- MEAGHER, E. P., TOSSELL, J. A. & GIBBS, G. V. (1979). *Phys. Chem. Miner.* **4**, 11–21.
- PAULING, L. (1933). *Z. Kristallogr.* **84**, 442–452.
- SAS User's Guide* (1979). Raleigh: SAS Institute.
- SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925–946.
- TURCO, G. (1962). *Bull. Soc. Fr. Minéral. Cristallogr.* **85**, 407–458.
- VERMAAS, F. H. S. (1952). *Am. Mineral.* **37**, 960–965.
- WELLS, A. F. (1975). *Structural Inorganic Chemistry*, 4th ed., p. 435. Oxford: Clarendon Press.
- ZAGALSKAYA, YU. G. & BELOV, N. V. (1964). *Sov. Phys. Crystallogr.* **8**, 429–432.

Acta Cryst. (1982). **B38**, 401–408

Hydrogen Bonds in $\text{Na}_3\text{AsS}_4 \cdot 8\text{D}_2\text{O}$: Neutron Diffraction, X-ray Diffraction and Vibrational Spectroscopic Studies

BY K. MEREITER AND A. PREISINGER

Institut für Mineralogie, Kristallographie und Strukturchemie, Technische Universität Wien, A-1060 Wien, Austria

O. BAUMGARTNER AND G. HEGER

Kernforschungszentrum Karlsruhe GmbH, Institut für Angewandte Kernphysik I, D-7500 Karlsruhe, Federal Republic of Germany

AND W. MIKENDA AND H. STEIDL

Institut für Organische Chemie der Universität Wien, A-1090 Wien, Austria

(Received 11 February 1981; accepted 12 August 1981)

Abstract

The structure of $\text{Na}_3\text{AsS}_4 \cdot 8\text{D}_2\text{O}$ has been refined from neutron data to $R = 0.052$ for 2144 reflections and from X-ray data to $R = 0.022$ for 3310 reflections. It crystallizes in space group $P2_1/c$, with $a = 8.683$ (2), $b = 12.979$ (2), $c = 13.702$ (2) Å, $\beta = 103.40$ (1)° and $Z = 4$. The structure consists of $\text{Na}(\text{D}_2\text{O}, \text{S})_6$ octahedra and AsS_4 tetrahedra which are linked to form corrugated layers parallel to (010), with the composition $\text{Na}_3\text{AsS}_4 \cdot 8\text{D}_2\text{O}$. Fifteen different D atoms of the structure form one O–D...O bond ($\text{D}\cdots\text{O} = 1.906$ Å), thirteen approximately linear O–D...S bonds ($\text{D}\cdots\text{S} = 2.248$ – 2.551 Å) and one bifurcated O–D...S,S bond ($\text{D}\cdots\text{S} = 2.732$ and 2.768 Å). The sixteenth D atom, D(32), is surrounded by one O and two S atoms at distances $\text{D}\cdots\text{O} = 2.798$, $\text{D}\cdots\text{S} = 3.213$ and 3.195 Å that are far outside the range

usually thought to indicate hydrogen bonding. Single-crystal Raman spectra were measured in the range $T = 295$ – 75 K on the D_2O , H_2O and isotopically dilute HDO variants of the title compound. With one exception the uncoupled O–D(H) stretching frequencies were in the range $\tilde{\nu} = 2430$ – 2580 (3270 – 3490) cm^{-1} . Reasonable assignments of these frequencies to the 15 different hydrogen-bonded O–D(H) groups are presented. An additional O–D(H) stretching frequency observed at $\tilde{\nu} = 2664$ (3618) cm^{-1} is due to O–D(H) (32) and shows that this group has very weak, but not negligibly small, interactions with the surrounding atoms.

Introduction

This study was stimulated by our interest in hydrogen bonds between water molecules and sulfur in crystalline

hydrates (Mereiter, Preisinger & Guth, 1979; Mikenda & Preisinger, 1980). In this paper we report the results of a study by single-crystal neutron and X-ray diffraction of the structure of Na₃AsS₄·8D₂O, which was previously determined for the H compound by Dittmar & Schäfer (1978). The present study confirms the earlier work concerning the heavy atoms, but provides improved precision for them and in addition accurate locations for the D atoms. Our study has been supplemented by Raman measurements.

Crystal growth

Large crystals of Na₃AsS₄·8(H, D)₂O with 0, 5, 95 and >99.5% deuteration were grown from saturated solutions of sodium thioarsenate in the appropriate H₂O–D₂O mixtures by controlled slow cooling. Well thermostated closed vessels of 100 ml capacity and temperatures in the range 318–313 K with cooling rates of about 0.2 K per day yielded prismatic crystals of up to 6 cm length. Na₃AsS₄·8H₂O and Na₃AsS₄·8D₂O were prepared from Na₂S, As₂S₃ and S with either H₂O or D₂O (*Gmelins Handbuch der anorganischen Chemie*, 1928).

Neutron diffraction measurements and refinement

A crystal of Na₃AsS₄·8D₂O, cut to a cube, edge length 4 mm, and quenched several times with liquid nitrogen to reduce extinction effects, was mounted on the four-circle neutron diffractometer P3 at the research reactor FR2, Kernforschungszentrum Karlsruhe. A neutron beam with $\lambda_w = 0.895 \text{ \AA}$ and $\omega/2\theta$ scans (scan width 1.4–3.2°, scan speed 1° min⁻¹) were used to measure the intensities of about 5000 reflections with $(\sin \theta)/\lambda < 0.7 \text{ \AA}^{-1}$. After averaging of symmetry-equivalent reflections, 4124 independent data were obtained [$\sum (\langle I \rangle - I) / \sum \langle I \rangle = 0.024$]. Because the material was fully deuterated, absorption was small and ignored.

The positions of the D atoms were obtained from a Fourier synthesis based on the heavy-atom parameters from the X-ray study. The subsequent least-squares refinement with anisotropic temperature factors for all atoms and an isotropic extinction correction converged for the 2144 reflections with $F_o > 5\sigma(F_o)$ to $R = 0.052$ and $R_w = 0.043$, where $w = 1/\sigma^2(F_o)$. The largest correction for extinction was a factor of 0.75 for the 104 reflection. The coherent scattering lengths used were those of Koester (1977). Final atomic coordinates are listed in Table 1.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36378 (54 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^5$) and equivalent isotropic thermal parameters (\AA^2)

The neutron values are listed above the X-ray values. The X-ray parameters of the D atoms were obtained by refining rigid D₂O molecules. The e.s.d.'s of the D₂O rotation angles average 2.1°. The common isotropic temperature factor for all D's refined to 5.4 (2) \AA^2 . $B_{eq} = \frac{2}{3}\pi^2 (U_{11} + U_{22} + U_{33})$.

	x	y	z	B _{eq}
Na(1)	0	0	0	2.51 (19)
	0	0	0	2.76 (5)
Na(2)	50000	50000	0	2.61 (19)
	50000	50000	0	2.69 (5)
Na(3)	33786 (38)	55102 (26)	40885 (24)	2.37 (13)
	33769 (9)	55092 (6)	40865 (6)	2.56 (3)
Na(4)	82931 (41)	5993 (27)	41629 (24)	2.58 (13)
	82913 (10)	5971 (6)	41622 (6)	2.75 (3)
As	71371 (17)	67100 (11)	25173 (11)	1.40 (5)
	71395 (2)	67090 (1)	25190 (1)	1.51 (1)
S(1)	78796 (43)	51244 (28)	28607 (25)	1.63 (13)
	78768 (6)	51246 (4)	28642 (4)	1.95 (2)
S(2)	60741 (50)	68916 (30)	9533 (28)	2.00 (15)
	60789 (6)	68932 (4)	9518 (4)	2.20 (2)
S(3)	54835 (49)	71230 (32)	34178 (30)	2.32 (16)
	54866 (6)	71233 (4)	34131 (4)	2.53 (2)
S(4)	92022 (47)	77124 (31)	28591 (29)	2.05 (15)
	91949 (6)	77087 (4)	28557 (4)	2.21 (2)
O(1)	19526 (28)	10393 (19)	95872 (19)	2.85 (9)
	19527 (19)	10337 (11)	95914 (12)	3.08 (7)
O(2)	14931 (26)	84927 (17)	96617 (18)	2.51 (8)
	14888 (19)	84981 (11)	96627 (12)	2.79 (6)
O(3)	73950 (29)	40271 (20)	6587 (17)	2.76 (10)
	73931 (20)	40236 (12)	6550 (11)	2.96 (7)
O(4)	40980 (27)	46005 (17)	14573 (17)	2.31 (8)
	40900 (17)	46034 (11)	14536 (11)	2.61 (6)
O(5)	53115 (25)	42637 (18)	41107 (16)	2.40 (8)
	53093 (17)	42688 (11)	41086 (11)	2.66 (6)
O(6)	14567 (28)	51950 (19)	25113 (16)	2.57 (9)
	14605 (18)	51933 (12)	25085 (11)	2.88 (6)
O(7)	78800 (33)	23483 (19)	35013 (19)	3.01 (10)
	78811 (21)	23432 (13)	35099 (11)	3.27 (7)
O(8)	9141 (27)	11026 (19)	50096 (18)	2.64 (9)
	9119 (18)	11023 (12)	50086 (12)	2.89 (6)
D(11)	18508 (40)	15270 (21)	90706 (24)	5.95 (15)
	17667	15221	90505	
D(12)	26592 (32)	13573 (22)	101410 (22)	4.84 (13)
	25892	14099	101430	
D(21)	7316 (26)	81079 (18)	91744 (17)	3.45 (9)
	7532	80961	91803	
D(22)	17154 (28)	80978 (18)	102694 (18)	3.67 (9)
	17391	80938	102655	
D(31)	77030 (31)	43219 (23)	13153 (18)	4.42 (11)
	77352	43011	13195	
D(32)	71293 (53)	33554 (27)	7569 (27)	7.21 (20)
	71145	33204	7472	
D(41)	49687 (35)	48187 (22)	19606 (19)	4.56 (12)
	50208	47942	19492	
D(42)	40763 (28)	38682 (19)	15277 (18)	3.71 (10)
	41115	38639	14621	
D(51)	60762 (27)	44132 (20)	37223 (17)	3.90 (10)
	60649	44308	37192	
D(52)	49836 (29)	35625 (19)	39826 (18)	3.69 (10)
	49548	35749	39513	
D(61)	4207 (28)	53077 (21)	26124 (17)	4.07 (11)
	4674	53486	26699	
D(62)	14791 (32)	44544 (21)	24477 (18)	4.11 (11)
	14681	44537	25194	

Table 1 (*cont.*)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
D(71)	68917 (35) 68646	23296 (22) 23245	30225 (21) 30480	4.57 (13)
D(72)	86718 (37) 86193	24332 (23) 24534	31230 (21) 30958	4.95 (13)
D(81)	17081 (30) 16799	13681 (19) 13989	46900 (19) 46881	3.98 (10)
D(82)	9715 (29) 9599	15420 (19) 14993	55790 (19) 56061	3.91 (11)

X-ray diffraction measurements and refinement

Cell dimensions and reflection intensities were measured on a Philips PW 1100 four-circle diffractometer with graphite-monochromatized Mo *K* α radiation. The cell parameters of both the H and the D compounds were determined by least-squares refinement from the 2θ values of about 90 reflections (Table 2). A crystal sphere of Na₃AsS₄·8D₂O, diameter 0.28 mm, was used for data collection in the $\omega/2\theta$ scan mode (scan width 1.4°, scan speed 2° min⁻¹). One half of reciprocal space with $(\sin \theta)/\lambda < 0.7 \text{ \AA}^{-1}$ was measured. The 8622 measurements were averaged to 4410 symmetry-independent intensities of which 3310 with $I > 3\sigma(I)$ were used for further calculations. $\sum (\langle I \rangle - I) / \sum \langle I \rangle$ was 0.023. The data were corrected for absorption ($\mu R = 0.40$).

Full-matrix least-squares refinement, started with the parameters given by Dittmar & Schäfer (1978), converged to $R = 0.029$ with anisotropic temperature factors and an isotropic correction for extinction. The approximate positions of the D atoms were obtained from a difference map. In the subsequent calculations the D atoms were refined as parts of rigid D₂O molecules with D–O–D = 102.1–107.8° (angle calculated from the equation D–O–D = 91.5° + 0.129 × A–O–A, where A–O–A is the acceptor–oxygen–acceptor angle of the corresponding molecule), O–D = 0.96 Å for the nuclear D position and O–D = 0.80 Å for the center of the usual spherical scattering function of H. A common isotropic temperature factor was used for all D atoms. The final refinement converged with weights $w = 1/[\sigma^2(F_o) + 0.0003 \times F_o^2]$ to $R = 0.022$ and $R_w = 0.026$. The largest correction for extinction was a factor of 0.95

Table 2. *Crystal data at room temperature*

	Na ₃ AsS ₄ ·8H ₂ O	Na ₃ AsS ₄ ·8D ₂ O
Space group $P2_1/c$, $Z = 4$		
<i>a</i>	8.682 (2) Å	8.683 (2) Å
<i>b</i>	12.967 (2)	12.979 (2)
<i>c</i>	13.692 (2)	13.702 (2)
β	103.39 (1)°	103.40 (1)°
<i>V</i>	1499.5 Å ³	1502.1 Å ³
<i>M_r</i>	416.3	432.4
<i>D_c</i>	1.84 Mg m ⁻³	1.91 Mg m ⁻³

for the 104 reflection. Complex neutral-atom scattering functions were used (*International Tables for X-ray Crystallography*, 1974). Final atomic coordinates are given in Table 1.*

Comparison of X-ray and neutron results

The cell dimensions of Na₃AsS₄·8H₂O (Table 2) agree well with those of Rémy & Bachet (1968), but differ significantly from those given by Dittmar & Schäfer (1978) [$a = 8.651$ (3), $b = 12.995$ (4), $c = 13.596$ (5) Å and $\beta = 102.77$ (7)°] who derived them from a Guinier powder photograph. The atomic coordinates given by Dittmar & Schäfer (1978), however, agree well with those obtained here (maximum difference with our neutron and X-ray parameters: 0.03 Å or 3.4 pooled e.s.d.'s). As Dittmar & Schäfer investigated the H compound some of the differences could be due to an isotope effect, but the pooled e.s.d.'s are too large to draw a reliable conclusion. The cell parameters of the H and the D compounds show only a small isotope effect (Table 2).

The agreement between our neutron and X-ray positional parameters is good. The distances between corresponding neutron and X-ray positions of Na, As, S and O are on average 0.006 Å and at most 0.013 Å. Half-normal probability plots of the weighted differences between the atomic coordinates (Abrahams & Keve, 1971) showed a slope of 1.0 for Na, As and S, and a slope of 1.8 (δ_p max = 3.9) for the O atoms. The X-ray O positions are systematically shifted off the D atoms towards the Na⁺ ions, by an average of 0.005 Å with respect to the neutron positions. These shifts are most likely due to bonding effects (Bats, Coppens & Koetzle, 1977), and therefore interatomic distances and angles were calculated from the X-ray coordinates of Na, As and S, and from the neutron coordinates of O and D, except for Table 4, where X-ray-only values are also given. This table shows that the X-ray refinement of rigid water molecules yields results for distances and angles which could be quite useful in cases where neutron data are not at hand.

For the anisotropic temperature factors of Na, As, S and O there are systematic differences between neutron and X-ray values, the former being on average 0.83 times smaller than the latter. The ellipsoids of vibration, however, are very similar in terms of orientation and shape.

The structure

The structure of Na₃AsS₄·8D₂O is dominated by layers of Na coordination octahedra (Figs. 1 and 2,

* See previous footnote.

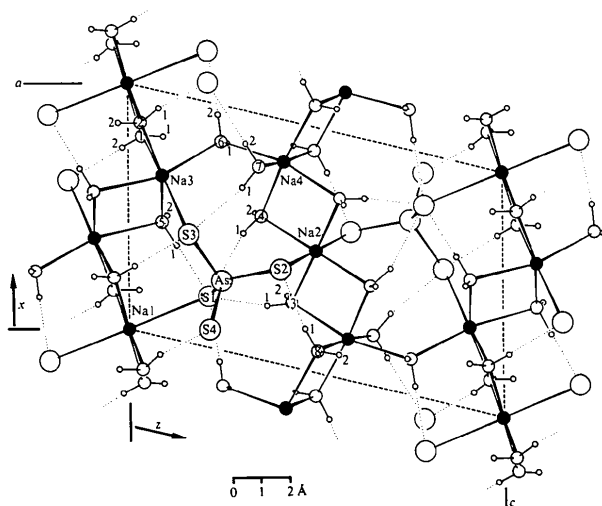


Fig. 1. (010) projection of a $\text{Na}_3\text{AsS}_4 \cdot 8\text{D}_2\text{O}$ layer at $y \sim 0$. The smallest circles are D atoms, the next smallest circles O atoms. D atoms are labeled by the last digit of the atomic numbering. The dotted lines show exclusively intralayer hydrogen bonds.

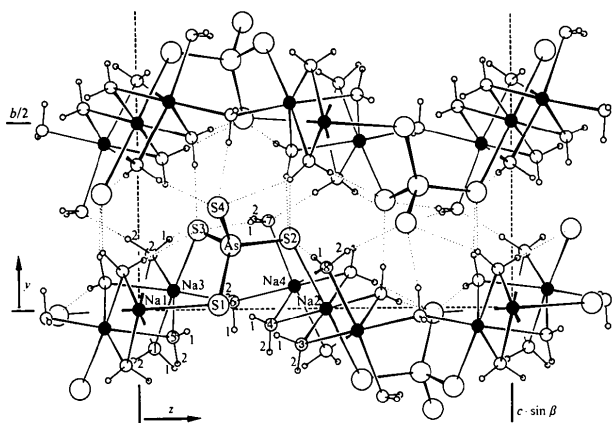


Fig. 2. The structure of $\text{Na}_3\text{AsS}_4 \cdot 8\text{D}_2\text{O}$ projected along *a*. Dotted lines show intra- and interlayer hydrogen bonds. The same atoms as in Fig. 1 are labeled.

Table 3). It contains four different Na^+ ions, of which Na(1) and Na(2) are surrounded by four D_2O and two S, Na(3) by five D_2O and one S, and Na(4) by six D_2O . Each Na(1) and Na(2) octahedron shares a pair of parallel edges and each Na(3) and Na(4) octahedron a pair of non-parallel edges with two neighboring Na octahedra; in all cases the edges are defined by pairs of D_2O molecules. In this way two very similar, but independent, $\text{Na}-\text{D}_2\text{O}$ zigzag chains are formed. These two chains lie parallel to *a* at $y \sim 0$, $z \sim 0$ and at $y \sim 0$, $z \sim \frac{1}{2}$, and are linked parallel to *c* forming a sheet by corner-sharing *via* $\text{D}_2\text{O}(6)$. The AsS_4 tetrahedra are anchored in both sides of this sheet by sharing three of their four S atoms with the Na octahedra, while each fourth S atom protrudes from the sheet. Thus parallel

Table 3. Interatomic distances (Å) and angles ($^\circ$) calculated from the X-ray parameters of Na, As and S, and from the neutron parameters of O

(a) Na^+ ions

Na(1)—S(1) $\times 2$	3.080 (1)	Na(2)—S(2) $\times 2$	2.837 (1)
—O(1) $\times 2$	2.336 (3)	—O(3) $\times 2$	2.422 (3)
—O(2) $\times 2$	2.450 (3)	—O(4) $\times 2$	2.365 (3)
Na(3)—S(3)	3.063 (2)	Na(4)—O(3)	2.406 (3)
—O(1)	2.536 (3)	—O(4)	2.425 (3)
—O(2)	2.361 (3)	—O(6)	2.411 (3)
—O(5)	2.326 (3)	—O(7)	2.442 (3)
—O(5)	2.486 (3)	—O(8)	2.396 (3)
—O(6)	2.437 (3)	—O(8)	2.504 (3)

(b) AsS_4 tetrahedron

		S—As—S	
As—S(1)	2.173 (1)	S(1)—S(2)	3.560 (1) 111.09 (3)
—S(2)	2.145 (1)	—S(3)	3.511 (1) 108.25 (3)
—S(3)	2.160 (1)	—S(4)	3.545 (1) 109.49 (3)
—S(4)	2.168 (1)	S(2)—S(3)	3.540 (1) 110.65 (3)
		—S(4)	3.460 (1) 106.72 (3)
		S(3)—S(4)	3.559 (1) 110.66 (3)

to (010) the structure consists of corrugated layers of composition $\text{Na}_3\text{AsS}_4 \cdot 8\text{D}_2\text{O}$. The layers are reinforced by nine independent intralayer hydrogen bonds; they are stacked above each other by the *c*-glide planes and are interconnected by six independent interlayer hydrogen bonds.

Bond distances within the four different Na octahedra are in the usual range, 2.326–2.536 Å for Na—O and 2.837–3.080 Å for Na—S. Na(1) and Na(2) are located at centers of symmetry. Their coordination octahedra are quite regular with respect to the bond angles (6.2 and 6.7° maximum deviations, respectively, from the ideal values 90 and 180°). The $\text{Na}(3)\text{O}_5\text{S}$ and $\text{Na}(4)\text{O}_6$ octahedra are more distorted, having bond angles which deviate up to 21.5 and 19.1°, respectively, from the ideal values 90 and 180°.

With As—S bonds of 2.145–2.173 Å and S—As—S angles of 106.7–111.1° the AsS_4 tetrahedron is moderately distorted. Three each of the four S atoms are bonded to one Na and accept in addition three to four hydrogen bonds. The fourth S atom is not bonded to Na. It protrudes from one $\text{Na}_3\text{AsS}_4 \cdot 8\text{D}_2\text{O}$ layer in the direction of the next and accepts two intra- and three interlayer hydrogen bonds.

Water molecules and hydrogen bonds

Bond distances and angles for the water molecules are given in Table 4. Seven water molecules bridge pairs of Na^+ ions. The Na—O distances range from 2.326 to 2.536 Å, but are, if separately averaged for each water molecule, more constant, varying only from 2.395 to 2.450 Å. The molecules $\text{D}_2\text{O}(1)$ through $\text{D}_2\text{O}(5)$ and $\text{D}_2\text{O}(8)$, which define the shared edges between the Na octahedra, have quite uniform Na—O—Na angles close to 90°, varying from 89.8 to 96.3°. $\text{D}_2\text{O}(6)$, however,

Table 4. *Hydrogen bonds and geometry of the water molecules (values in Å and deg)*

Values on each first line were calculated from the X-ray parameters of Na and S, and from the neutron parameters of O and D. Those on each second line were calculated exclusively from the X-ray parameters; O—D = 0.96 Å and D—O—D = 102.1–107.8° were fixed during the rigid-body refinement of the D₂O molecules. Least-squares standard deviations are: A—C and A—L, 0.002 Å; ∠CAC' and ∠LAL', 0.1°. The average e.s.d. of the remaining figures is estimated as: A—B, 0.01; B—C, 0.013 Å; ∠BAC, 2; ∠ABC, 3 and ∠BAB', 0.7°.

A	B	C	A—B	B—C	A—C	∠BAC	∠ABC	∠BAB'	∠CAC'	L	A—L	∠LAL'
O(1)—D(11)...	S(2)		0.938 (4)	2.732 (4)	3.355 (3)	42.1 (3)	124.6 (3)	103.9 (4)	64.9 (1)	Na(1)	2.336 (3)	92.0 (1)
			0.96	2.781	3.362	46	120	103.6	64.8		2.330	92.2
	...S(4)			2.768 (4)	3.646 (3)	18.0 (3)	156.0 (3)		122.9 (1)	Na(3)	2.536 (3)	
					2.740	3.654	15	159		122.7		2.533
	—D(12)...	S(3)	0.952 (4)	2.455 (3)	3.407 (3)	1.3 (2)	178.2 (3)					
					0.96	2.456	3.406	7	170			
O(2)—D(21)...	S(4)		0.963 (3)	2.248 (3)	3.201 (3)	6.7 (2)	170.4 (3)	107.0 (3)	112.6 (1)	Na(1)	2.450 (3)	93.6 (1)
			0.96	2.253	3.204	7	170	106.1	112.3		2.442	93.8
	—D(22)...	O(7)	0.959 (4)	1.906 (4)	2.864 (4)	1.3 (2)	178.0 (3)			Na(3)	2.361 (3)	
					0.96	1.902	2.860	3	176			2.360
O(3)—D(31)...	S(1)		0.957 (4)	2.338 (3)	3.279 (3)	8.8 (2)	167.7 (3)	105.5 (4)		Na(2)	2.422 (3)	89.8 (1)
			0.96	2.349	3.285	11	165	105.3			2.422	89.8
	—D(32)		0.920 (5)		See below					Na(4)	2.406 (3)	
											2.403	
O(4)—D(41)...	S(1)		0.941 (4)	2.573 (3)	3.466 (3)	15.7 (3)	158.6 (3)	104.9 (3)	94.9 (1)	Na(2)	2.365 (3)	90.7 (1)
			0.96	2.543	3.473	12	163	103.8	94.7		2.363	90.9
	—D(42)...	S(3)	0.956 (4)	2.295 (3)	3.236 (3)	8.5 (2)	167.9 (3)			Na(4)	2.425 (3)	
					0.96	2.286	3.240	5	172			2.417
O(5)—D(51)...	S(1)		0.962 (4)	2.352 (3)	3.300 (3)	8.2 (2)	168.4 (3)	107.7 (4)	126.1 (1)	Na(3)	2.326 (3)	95.4 (1)
			0.96	2.348	3.297	7	170	107.8	126.0		2.321	95.5
	—D(52)...	S(2)	0.958 (4)	2.365 (3)	3.299 (3)	10.7 (2)	165.0 (3)			Na(3)	2.486 (3)	
					0.96	2.375	3.305	12	163			2.488
O(6)—D(61)...	S(1)		0.953 (4)	2.326 (3)	3.256 (3)	10.4 (2)	165.3 (3)	101.9 (4)	81.9 (1)	Na(3)	2.437 (3)	127.7 (1)
			0.96	2.344	3.261	15	160	102.1	81.9		2.438	127.9
	—D(62)...	S(4)	0.966 (4)	2.353 (3)	3.295 (3)	10.8 (2)	164.8 (3)			Na(4)	2.411 (3)	
					0.96	2.364	3.293	12	163			2.406
O(7)—D(71)...	S(3)		0.952 (4)	2.515 (3)	3.458 (3)	6.6 (3)	170.9 (4)	106.0 (4)	101.4 (1)	Na(4)	2.442 (3)	100.1 (1)
			0.96	2.520	3.465	9	168	104.6	101.1		2.432	100.6
	—D(72)...	S(4)	0.959 (5)	2.551 (4)	3.509 (4)	1.2 (3)	178.3 (3)			O(2)	2.864 (4)	
					0.96	2.561	3.518	4	174			2.860
O(8)—D(81)...	S(2)		0.962 (4)	2.390 (3)	3.347 (3)	5.3 (2)	172.5 (3)	104.5 (4)	112.8 (1)	Na(4)	2.396 (3)	96.3 (1)
			0.96	2.400	3.348	8	169	106.1	112.8		2.394	96.3
	—D(82)...	S(4)	0.958 (4)	2.390 (3)	3.328 (3)	10.0 (2)	166.0 (3)			Na(4)	2.504 (3)	
					0.96	2.377	3.329	6	171			2.504

O and S atoms neighboring D(32)

	Distance		Distance	∠O,S—D(31)—O,S		Distance	∠O,S—D(31)—O,S
D(32)—O(3)	0.920 (5)	O(3)—O(2)	3.467 (4)	130.5 (4)	O(2)—S(2)	4.475 (3)	96.0 (5)
—O(2)	2.795 (5)	—S(2)	3.509 (3)	101.1 (5)	—S(3)	4.282 (3)	91.0 (5)
—S(2)	3.213 (5)	—S(3)	3.932 (3)	138.6 (5)	S(2)—S(3)	3.628 (1)	69.0 (5)
—S(3)	3.195 (5)						

which constitutes the only corner-sharing link between two Na octahedra, has a considerably larger Na—O—Na angle of 127.7°. In all these cases the electron lone pairs of the D₂O molecules are directed approximately towards the Na⁺ ions and the water molecule coordination is, according to Ferraris & Franchini-Angela's (1972) classification, of type *A*. Only D₂O(7) has a type *G* coordination and accepts bonds from Na(4) and D₂O(2). This latter is the only O—D...O-type hydrogen bond of the structure.

Thirteen of the D atoms are involved in approximately linear O—D...S hydrogen bonds, which are characterized by distances of 2.248–2.551 Å for D...S, 3.201–3.509 Å for O...S and O—D...S angles of 158.6–178.3°. The corresponding mean values are 2.369, 3.337 Å and 168.6°, respectively. All

these figures fit quite well into the presently known pattern of straight and unfurcated O—D(H)...S bonds, for which a range of O...S = 3.21–3.52 Å with a mean value of 3.32 Å was reported for 66 other cases, mainly from X-ray data (Mereiter *et al.*, 1979). As in Na₂S.9D₂O (Preisinger, Mereiter, Baumgartner, Heger, Mikenda & Steidl, 1981), Na₂S₂O₃.5H₂O (Lisensky & Levy, 1978) and Na₃SbS₄.9D₂O (Mereiter *et al.*, 1979) most of the straight O—D...S bonds in the title compound fall within a small range of lengths, 2.3–2.4 Å for D(H)...S and 3.25–3.4 Å for O...S. Only four of the straight O—D...S bonds in the title compound moderately exceed the larger figures.

D(11) is clearly involved in an almost symmetrically branched bifurcated hydrogen bond to two S atoms, which constitute an edge of the AsS₄ tetrahedron. The

second D atom of the $\text{D}_2\text{O}(1)$ molecule forms the usual straight $\text{O}-\text{D}\cdots\text{S}$ bond to a third sulfur. This situation closely resembles that found with the $\text{D}_2\text{O}(3)$ molecule in $\text{Na}_3\text{SbS}_4 \cdot 9\text{D}_2\text{O}$ (Mereiter *et al.*, 1979).

The nearest available proton acceptor atoms to D(32) are O(2), S(2) and S(3). The distances $\text{D}\cdots\text{O}(2) = 2.80$, $\text{D}\cdots\text{S}(2) = 3.21$ and $\text{D}\cdots\text{S}(3) = 3.20$ Å are about 0.4 Å larger than the sum of the van der Waals radii (H 1.0, O 1.4, S 1.8 Å) and thus far outside the hydrogen-bond range as defined by Hamilton & Ibers (1968). The number of salt hydrates, where H, D-acceptor distances exceed the sum of the van der Waals radii by so much, seems to be very limited and was, as far as we were aware, restricted to hydrated alkali salts of complex cyanides, *e.g.* $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ (Hamilton & Ibers, 1968; Falk & Knop, 1973; Bottomley & White, 1979), or $\text{Na}_2\text{Pt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$ (Johnson, Koch & Williams, 1977).

Bond lengths and angles of the D_2O molecules in the title compound depend on the coordination of the molecules. The O-D bonds, uncorrected for thermal motion, are in the range 0.920–0.966 Å, average 0.954 Å. The shortest O-D bonds are observed for the two D atoms with the largest D-acceptor distances, $\text{O}-\text{D}(32) = 0.920$ and $\text{O}-\text{D}(11) = 0.938$ Å, and which exhibit the largest thermal vibrations. Correction of the distances for thermal motion results, with the lower boundary correction, in $\text{O}-\text{D} = 0.944\text{--}0.970$ Å (average 0.959 Å) and, with the riding-motion model, in $\text{O}-\text{D} = 0.976\text{--}1.003$ Å (average 0.984 Å).

The D-O-D bond angles correlated nicely with the acceptor-O-acceptor angles ($A-O-A$). The smallest and largest D-O-D angles, 101.9° for O(6) and 107.7° for O(5), correspond to the smallest and largest acceptor angles, 81.9 and 126.1° , respectively. Such a correlation has already been shown to exist by Ferraris & Franchini-Angela (1972), but their equation $\text{D,H-O-D,H} = (96.0 + 0.107 \times A-O-A)^\circ$, derived from a very broad spectrum of hydrates with $M^{1+}\text{--}M^{6+}$ cations, predicts D-O-D angles for the thioarsenate which are on average about 2° larger than observed. Our regression analysis of D,H-O-D,H versus $A-O-A$ angles from data on twelve hydrated salts of Na determined by neutron diffraction gives $\text{D,H-O-D,H} = (91.5 + 0.129 \times A-O-A)^\circ$, which fits the values observed in the thioarsenate much better [for $\text{D}_2\text{O}(1)$ the average of the angles $\text{S}(2)\text{--O}(1)\text{--S}(3)$ and $\text{S}(4)\text{--O}(1)\text{--S}(3)$ was taken as $A-O-A$ (Table 4); for $\text{D}_2\text{O}(3)$ the angles D-O-D and $A-O-A$ are identical]. The r.m.s. deviation from the neutron values is 1° . These were the values used in the X-ray rigid-body least-squares refinement of the D_2O molecules.

Vibrational spectra

The Raman spectra of H_2O , D_2O and isotopically dilute HOD compounds were measured in the tem-

perature range 75–295 K (Kr-ion laser excitation at $\lambda = 647.1$ nm; Jarrel-Ash Raman spectrometer 25-300; Oxford Instruments CF 100 cryogenic unit). Only the O-D(H) stretching frequencies of the isotopically dilute samples will be discussed here; other aspects will be described elsewhere (Mikenda, Preisinger & Steidl, 1981). The technique of isotopic dilution exhibits considerable advantages with respect to hydrogen-bond investigations of crystalline hydrates, because inter- and intramolecular coupling effects between the O-D(H) oscillators largely disappear (Falk & Knop, 1973). The Raman measurements did not provide any evidence of significant structural changes in the title compound at decreasing temperatures. Room- and low-temperature spectra were almost identical, except for the usual effects of considerably decreased line widths and small frequency shifts at decreasing temperatures [$(\tilde{\nu}$ at 75 K)/ $(\tilde{\nu}$ at 295 K) < 1.05]. This is of importance for the subsequent discussion, because only room-temperature structural data are available, which can, however, be used without serious restrictions for the interpretation of the low-temperature spectra.

The range of O-D stretching frequencies of the Raman spectrum at 75 K of a sample with 5% D_2O + 95% H_2O is shown in Fig. 3(a) in a simplified way. Nine different lines, with frequencies as shown, could be identified; the corresponding frequencies of uncoupled O-H vibrations are given in brackets. Although the

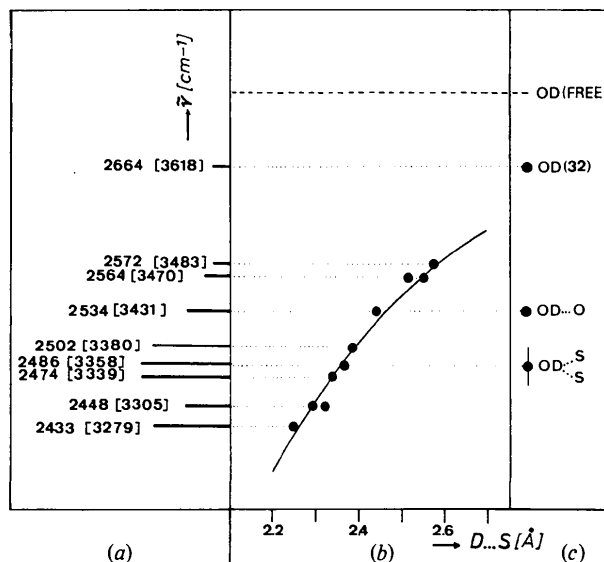


Fig. 3. (a) Raman spectrum (schematic) and frequencies of uncoupled OD oscillators at 75 K for $\text{Na}_3\text{AsS}_4 \cdot 8(\text{H},\text{D})_2\text{O}$. Uncoupled OH frequencies are given in brackets. (b) $\tilde{\nu}(\text{OD})$ versus distance $\text{D}\cdots\text{S}$ correlation for straight O-D \cdots S bonds. The solid line was obtained by a least-squares fit to the experimental points (see text). (c) Assignments of OD groups not involved in straight O-D \cdots S-type bonds. The uncertainty in the assignment of the OD group involved in a bifurcated hydrogen bond is indicated by a vertical bar.

spectra are very well resolved at 75 K (line widths $< 10 \text{ cm}^{-1}$) and the spectral resolution was fairly good (slit width $< 4 \text{ cm}^{-1}$) the number of lines is less than expected from the 16 non-equivalent O–D(H) groups. However, since the hydrogen-bond distances and angles of some O–D(H) groups are very similar, it is not unexpected that some of the line frequencies nearly coincide and the corresponding lines cannot be resolved.

A reasonable assignment scheme of the stretching frequencies to the different O–D(H) groups is shown in Fig. 3(b) and (c). The frequency of the O–D(22)···O bond can be estimated to a first approximation from literature data on $\text{O}_w\text{--D}\cdots\text{O}_w$ bonds (w denotes water O atoms), particularly from the data on hydrogen bonds in the different modifications of ice (Whalley, 1976). Corresponding to the distance $\text{D}(22)\cdots\text{O}(7) = 1.91 \text{ \AA}$, which may be slightly smaller at low temperatures, an uncoupled O–D frequency of about $\tilde{\nu} = 2540 \text{ cm}^{-1}$ is expected. Hence, the line at $\tilde{\nu} = 2534 \text{ cm}^{-1}$ fits this estimate very well. As described above, the O(3)–D(32) group is almost ‘free’ from a structural point of view. This group has a direct spectral correspondence in a high-frequency Raman line at $\tilde{\nu} = 2664 \text{ cm}^{-1}$, which is one of the highest O–D stretching frequencies observed so far in solid hydrates (Falk & Knop, 1973). The frequency shift relative to the frequency of free HOD, $\tilde{\nu} = 2727 \text{ cm}^{-1}$, is 63 cm^{-1} , which according to the Badger–Bauer rule (Badger & Bauer, 1937) would correspond to a hydrogen-bond strength of about 6 kJ mol^{-1} . However, since all distances to nearest-neighbor proton acceptors are larger than the sum of the van der Waals radii, the term ‘hydrogen bond’ is not appropriate if the frequently used geometrical criterion of Hamilton & Ibers (1968) is applied. The observed frequency shift should, therefore, be attributed in a more general way to the whole crystal field around the O–D(32) group, the main contributions arising from two S atoms and one water O atom (Table 4). The frequency of the line at $\tilde{\nu} = 2664 \text{ cm}^{-1}$ decreases slightly at increasing temperatures ($\tilde{\nu} = 2655 \text{ cm}^{-1}$ at 295 K). Such negative temperature coefficients, $\partial\tilde{\nu}/\partial T < 0$, are characteristic of highly bent or bifurcated hydrogen bonds (Falk, Huang & Knop, 1974), while the stretching frequencies of approximately linear bonds usually exhibit positive temperature coefficients. This latter behavior occurs with the three lines in the range $\tilde{\nu} = 2530\text{--}2580 \text{ cm}^{-1}$, while the temperature dependence of the remaining lines at $\tilde{\nu} < 2510 \text{ cm}^{-1}$ could not be established beyond doubt, due to the increasing line widths at increasing temperatures. Nevertheless, it can be concluded that the stretching frequency of the bifurcated O–D(11)···S,S bond must be below $\tilde{\nu} = 2510 \text{ cm}^{-1}$, which is the region of stretching frequencies of approximately linear O–D···S bonds with D···S distances of about 2.35 \AA . This closely corresponds with observations on

the bifurcated bond in $\text{Na}_3\text{SbS}_4 \cdot 9(\text{H,D})_2\text{O}$ whose stretching frequency was also found in the same region (Mikenda, Preisinger & Steidl, 1981).

For the remaining 13 almost linear O–D···S bonds, reasonable assignments are based on a monotonic frequency *versus* bond distance relationship. Although the detailed assignments are not unambiguous, the correlation diagram $\tilde{\nu}(\text{O–D})$ *versus* distance D···S, shown in Fig. 3(b), should not be significantly affected by possible errors. The deviations of the experimental points from the correlation curve $\tilde{\nu} = 2727 - 3.75 \times 10^4 \times \exp(-2.142 \times \text{distance D}\cdots\text{S})$, which was obtained by a least-squares fit to the experimental points according to Berglund, Lindgren & Tegenfeldt (1978), are $< \pm 20 \text{ cm}^{-1}$ (r.m.s. deviation 2.2 cm^{-1}). Since the plot (Fig. 3b) includes only proton donors of the same type, *i.e.* water molecules, as well as proton acceptors of the same type, *i.e.* S atoms of the AsS_4 group, the deviations from the fitted correlation curve should be due only to factors like bond angles, slight differences in the coordination of the water molecules, *etc.* Although very little is known about the quantitative frequency dependence on these factors, a scatter of $\pm 20 \text{ cm}^{-1}$ seems reasonable. This is confirmed by the correlation diagrams obtained for the different modifications of ice (Whalley, 1976), for $\text{Na}_2\text{S} \cdot 9(\text{H,D})_2\text{O}$ (Preisinger *et al.*, 1981) and for $\text{Na}_3\text{SbS}_4 \cdot 9(\text{H,D})_2\text{O}$ (Mikenda *et al.*, 1981) where similar scatters occur. It should be noted that the correlation curve of $\text{Na}_3\text{AsS}_4 \cdot 8(\text{H,D})_2\text{O}$ is somewhat below that of $\text{Na}_3\text{SbS}_4 \cdot 9(\text{H,D})_2\text{O}$ ($> 20 \text{ cm}^{-1}$), but significantly above that of $\text{Na}_2\text{S} \cdot 9(\text{H,D})_2\text{O}$ ($> 100 \text{ cm}^{-1}$). This shows the strong dependence of the O–D(H) frequencies on the net charge of the acceptor, which is certainly higher in the sulfide than in the thioarsenate and the thioantimonate. Consequently hydrogen-bond strengths cannot be estimated from the bond distance alone, because other parameters, like the net charge of the acceptor atom must also be taken into account. Further investigations are in progress to obtain a more complete view of this feature.

We thank Professor Dr J. Derkosch for helpful discussions. This work was supported by the Fonds zur Förderung der wissenschaftlichen Forschung (projects 2178 and 3743). Crystallographic calculations were performed mainly with XRAY-72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) and SHELX-76 (Sheldrick, 1976) at the Interuniversitäres Rechenzentrum Wien.

References

- ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157–165.
 BADGER, R. M. & BAUER, S. H. (1937). *J. Chem. Phys.* **5**, 839–851.

- BATS, J. W., COPPENS, P. & KOETZLE, T. F. (1977). *Acta Cryst.* B33, 37–45.
- BERGLUND, B., LINDGREN, J. & TEGENFELDT, J. (1978). *J. Mol. Struct.* 43, 179–185.
- BOTTOMLEY, F. & WHITE, P. S. (1979). *Acta Cryst.* B35, 2193–2195.
- DITTMAR, G. & SCHÄFER, H. (1978). *Z. Naturforsch. Teil B*, 33, 678–681.
- FALK, H., HUANG, C. & KNOP, O. (1974). *Can. J. Chem.* 52, 2380–2388.
- FALK, H. & KNOP, O. (1973). *Water, a Comprehensive Treatise*, edited by F. FRANKS, Vol. 2, pp. 55–113. New York: Plenum Press.
- FERRARIS, G. & FRANCHINI-ANGELA, M. (1972). *Acta Cryst.* B28, 3572–3583.
- Gmelins Handbuch der anorganischen Chemie* (1928). *Natrium*, System Nr. 21, 8th ed., pp. 958–960. Berlin: Verlag Chemie.
- HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*. New York: Benjamin.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, P. L., KOCH, T. R. & WILLIAMS, J. M. (1977). *Acta Cryst.* B33, 1976–1979.
- KOESTER, L. (1977). *Springer Tracts in Modern Physics – Neutron Physics*. Berlin: Springer.
- LISENSKY, G. C. & LEVY, H. A. (1978). *Acta Cryst.* B34, 1975–1977.
- MEREITER, K., PREISINGER, A. & GUTH, H. (1979). *Acta Cryst.* B35, 19–25.
- MIKENDA, W. & PREISINGER, A. (1980). *Spectrochim. Acta Part A*, 36, 365–370.
- MIKENDA, W., PREISINGER, A. & STEIDL, H. (1981). *J. Raman Spectrosc.* Submitted.
- PREISINGER, A., MEREITER, K., BAUMGARTNER, O., HEGER, G., MIKENDA, W. & STEIDL, H. (1981). *Inorg. Chim. Acta*. In the press.
- RÉMY, F. & BACHET, B. (1968). *Bull. Soc. Chim. Fr.* pp. 3568–3569.
- SHELDRIK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- WHALLEY, E. (1976). *The Hydrogen Bond*, Vol. 3, edited by P. SCHUSTER, G. ZUNDEL & C. SANDORFY, ch. 29, pp. 1426–1470. Amsterdam: North Holland.

Acta Cryst. (1982). B38, 408–415

The Electronic Factors Linking the Structures of Graphite, Arsenic and Selenium

BY JEREMY K. BURDETT* AND JUNG-HUI LIN

Department of Chemistry, The University of Chicago, Chicago, Illinois 60637, USA

(Received 15 October 1980; accepted 4 August 1981)

Abstract

The electronic structures of the graphite, arsenic and selenium arrangements are correlated with those of 'isoelectronic' molecules. The structural changes along the series are viewed in terms of simple molecular-orbital arguments, specifically the response of a parent structure to the presence of extra electrons (C → As → Se). Because of the extra symmetry present in the solid, the electronic explanation of the occurrence of puckered arsenic sheets is somewhat different from that used to view the trigonal pyramidal structure of ammonia.

Introduction

One of the successes of modern theoretical chemistry has been the methodical analysis of the molecular-orbital structures of molecules (Gimarc, 1979; Hoffmann, 1981) and the development of simple ideas and theories to view structural, chemical and frequently mechanistic questions from a global viewpoint (Hoffmann & Woodward, 1970; Mingos, 1977; Burdett, 1980*b*). Much of this research has used approximate molecular-orbital methods such as the extended Hückel method (Hoffmann, 1963; Hoffmann & Lipscomb, 1962*a,b*) and the various 'NDO' schemes (Dewar, 1969). By way of contrast there is a scarcity of similar electronic descriptions of structural aspects of solids. Until recently these were limited to valence-bond arguments for tetrahedrally based molecules and

* Fellow of the Alfred P. Sloan Foundation and Camille and Henry Dreyfus Teacher-Scholar.