JOURNAL OF SOLID STATE CHEMISTRY **70**, 225–228 (1987)

The Crystal Structure of $NaAs_4O_6Br$*

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Received December 15, 1986

The crystal structure of $NaAs_4O_6Br$ [a = 5.237(1), b = 8.043(1), c = 18.978(2) Å; space group $Pmcn$-D_{2h}^{16}; Z = 4] was solved by a direct method strategy and was refined to an R value of 0.038 for 1515 intensities and 68 variables. The structure is characterized by neutrally charged and slightly waved As_2O_3 sheets arranged parallel to (001). These sheets are combined by the Na and Br atoms. The Na atom is coordinated to nine oxygen atoms and one bromine atom and the Br atom is coordinated to six arsenic atoms and one sodium atom. The compound $NaAs_4O_6Br$ was synthesized by thermal treatment of NaBr and As_2O_3 in methanol solution [400(5) K, saturation vapor pressure].

Introduction

In connection with the syntheses of As(III)–oxygen compounds (*1*) parts of the system MeX–As_2O_3 (Me, alkali metal or a NH_4 group and X, halide) in methanol solution were investigated under moderate hydrothermal conditions. Up to 500 K, crystals of the two compounds $(NH_4Cl \cdot As_2O_3)_2 \cdot H_2O$ and $NaAs_4O_6Br$ were obtained. Whereas the structure of $(NH_4Cl \cdot As_2O_3)_2 \cdot H_2O$ was determined by (*2*), $NaAs_4O_6Br$ has not yet been mentioned in the literature.

Experimental

Crystals of $NaAs_4O_6Br$ were synthesized by the reaction of 2 g of an equimolar mixture of NaBr and As_2O_3 in a Teflon-lined vessel ($V \sim 8$ ml) with methanol (80% contents) as solvent. After heating at 400(5) K for 5 days and after subsequent slow cooling to room temperature for about 12 hr, colorless prismatic crystals of $NaAs_4O_6Br$ were obtained. They are elongated parallel to [100] showing the crystallographic forms {100} and {011}. It is worth mentioning that a modified insert with any alkali halide other than NaBr under the given experimental conditions does not yield a compound isotypic to $NaAs_4O_6Br$.

The size of the investigated crystals was 0.04 × 0.04 × 0.5 mm. Lattice parameters from 75 accurate 2θ values up to $2\theta = 40°$ as well as the X-ray intensities were collected with a STOE four-circle diffractometer AED2, using graphite monochromatized Mo$K\alpha$ radiation [a = 5.237(1), b = 8.043(1), c = 18.978(2) Å; space group $Pmcn$-D_{2h}^{16}; Z = 4]. The measurements were performed up to $\sin\theta/\lambda = 0.80$ Å^{-1} in the $2\theta/\omega$ scan mode. A minimum of 35 steps with respect to the α_1–α_2 splitting was used. The width

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* Dedicated to Dr. H. Nowotny.

0022-4596/87 $3.00

TABLE I

STRUCTURAL PARAMETERS FOR $NaAs_4O_6Br$ (STANDARD DEVIATIONS IN PARENTHESES)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
As(1)	$\frac{3}{4}$	0.16475(7)	0.88525(4)	190(2)	187(2)	174(3)	0	0	15(2)
As(2)	$\frac{3}{4}$	0.65321(7)	0.04713(4)	175(2)	178(2)	242(4)	0	0	−38(2)
As(3)	$\frac{3}{4}$	0.40912(7)	0.17856(4)	161(2)	179(2)	192(3)	0	0	3(2)
As(4)	$\frac{3}{4}$	0.78978(7)	0.83407(3)	155(2)	178(2)	185(3)	0	0	−9(2)
Br	$\frac{3}{4}$	0.49657(8)	0.71646(4)	243(2)	286(3)	318(4)	0	0	−96(3)
Na	$\frac{3}{4}$	0.4016(3)	0.5563(1)	302(13)	329(13)	241(16)	0	0	4(12)
O(1)	$\frac{3}{4}$	0.9467(5)	0.9036(2)	322(22)	167(17)	222(26)	0	0	−48(17)
O(2)	$\frac{1}{4}$	0.3902(4)	0.8607(2)	280(20)	166(16)	293(27)	0	0	36(18)
O(3)	0.0020(5)	0.6757(3)	0.8778(1)	164(11)	246(12)	187(15)	44(10)	33(12)	0(11)
O(4)	0.9972(5)	0.1949(3)	0.9512(1)	218(12)	319(13)	206(16)	−74(11)	−30(13)	51(12)

Note. The space group is $Pmcn\text{-}D_{2h}^{16}$. The Wyckoff number for the single atoms is $4c$, except that for the atoms O(3) and O(4), for which it is $8d$. ATF $= \exp(-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} 10^{-4} U_{ij} a_i^* a_j^* h_i h_j)$

of each step was 0.03° and the step time ranged from 0.5 to 1.5 sec per step. Three standard reflections were measured each 120 min and showed no significant variation in intensity during the measurement period. The X-ray intensities were corrected for absorption [ψ scan method, $\mu(\text{Mo}K\alpha) \sim 211\ \text{cm}^{-1}$] as well as for Lorentz and polarization effects. From the mean of 1921 unique data (406 with $F_o < 2\sigma F_o$) the crystal structure was solved by a direct method strategy combined with Fourier and difference Fourier summations and refined by least-squares techniques (68 variables). The final obtained R values are $R = 0.038$, resp., $R_w = 0.028$ with $w = [\sigma(F_o)]^{2-}$. All calculations were performed with complex scattering functions for neutral atoms (*3*) using the program system STRUCSY (Fa · STOE & Cie, Darmstadt, FRG) running on an Eclipse S 140. The structural parameters are listed in Table I. Some important interatomic distances are summarized in Table II.

Discussion

There are four crystallographically different As atom positions within the structure of $NaAs_4O_6Br$, but their coordination polyhedra (symmetry m) are quite similar. Each As atom is coordinated to three O atoms, forming a trigonal pyramid with the As atom at the apex. These coordination polyhedra are characteristic for trivalent arsenium (*1*, *4*) (arsenite groups). The As–O bonds vary from 1.778 to 1.826 Å; the O–As–O bond angles vary from 89.8 to 95.4°. The mean value of As–O bonds calculated from 75 representatives is 1.79 Å and the mean O–As–O angle, also calculated from 75 representatives, is 96° (*1*).

TABLE II

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR $NaAs_4O_6Br$ (STANDARD DEVIATIONS IN PARENTHESES)

Na–Br	= 3.134(2)	Br–Na	= 3.134(2)
O(1)	= 3.145(5)	As(3)	= 3.376(1) 2×
O(1′)	= 2.751(1) 2×	As(3′)	= 3.341(1)
O(3)	= 2.559(3) 2×	As(4)	= 3.247(1) 3×
O(4)	= 2.502(3) 2×		
O(4′)	= 2.708(3) 2×		
As(1)–O(1)	= 1.788(3)	O(1)–O(4)	= 89.8(1) 2×
O(4)	= 1.817(2) 2×	O(4)–O(4′)	= 90.9(2)
As(2)–O(2)	= 1.784(4)	O(2)–O(4)	= 96.6(1) 2×
O(4)	= 1.802(2) 2×	O(4)–O(4′)	= 94.6(2)
As(3)–O(2)	= 1.778(3)	O(2)–O(3)	= 95.4(1) 2×
O(3)	= 1.816(2) 2×	O(3)–O(3′)	= 91.3(2)
As(4)–O(1)	= 1.826(4)	O(1)–O(3)	= 91.1(1) 2×
O(3)	= 1.809(2) 2×	O(3)–O(3′)	= 93.7(2)

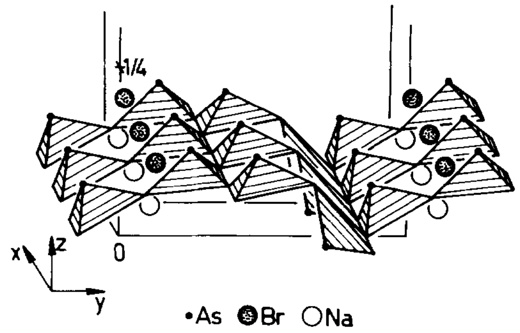

FIG. 1. A single As_2O_3 sheet in the field $0 < z < 1/4$ (the AsO_3 pyramids are shadowed). The Na and Br atoms are on the opposite sides of the sheet with approximately the same x and y parameters.

In a second coordination sphere the atom As(3) is coordinated to three Br atoms with As–Br = 3.34 Å (1×) and 3.38 Å (2×); the atom As(4) is also coordinated to three Br atoms with As–Br = 3.25 Å (3×). In both these cases the Br atoms complete the AsO_3 coordination polyhedra to distorted octahedra. A comparable feature was described for AsO_3 pyramids, where in some cases the coordination polyhedra of the As atom is completed by additional O atoms with As–O > 2.7 Å to distorted octahedra (*1*). The present structure determination indicates the possible completion of the As coordination in AsO_3 pyramids by halides. For the atoms As(1) and As(2) the next nearest neighbors are oxygen atoms with As–O > 3.2 Å.

The AsO_3 pyramids are connected via common O corner atoms to sheets in which the AsO_3 pyramids form six-membered rings. In Fig. 1 such an As_2O_3 sheet is shown in a projection. Three-fourths of the apices of the AsO_3 pyramids have the same orientation; the rest are in the opposite direction. Due to the space group *Pmcn* of the investigated crystal a stacking order of four equivalent sheets is observed. The Na and Br atoms are alternately located on both sides of these sheets: the Br atom lies near three As atoms and the Na atom on the side dominated by the O atoms. Each of the Na atoms is coordinated to nine O atoms and the Br atoms to six As atoms. The Na and the Br atoms are further connected by weak, more or less ionic interactions (Na–Br = 3.13 Å). The comparable value in cubic NaBr is 2.98 Å (*5*).

The coordination of the O(2) atoms differs from that of the three other O atoms. This atom O(2) is bonded to two As atoms and these As–O bonds are the shortest ones determined in $NaAs_4O_6Br$. The atoms O(1), O(3), and O(4) have in addition to the two As atoms one and two Na atom neighbors, respectively.

In four arsenites, neutrally charged As_2O_3 sheets have been determined before now. These compounds are two out of the three modifications of As_2O_3 (*6*, *7*) stable at room temperature: $NaAs_4O_6Br$ (this work) and $(NH_4Cl \cdot As_2O_3)_2 \cdot H_2O$ (*2*). In the first

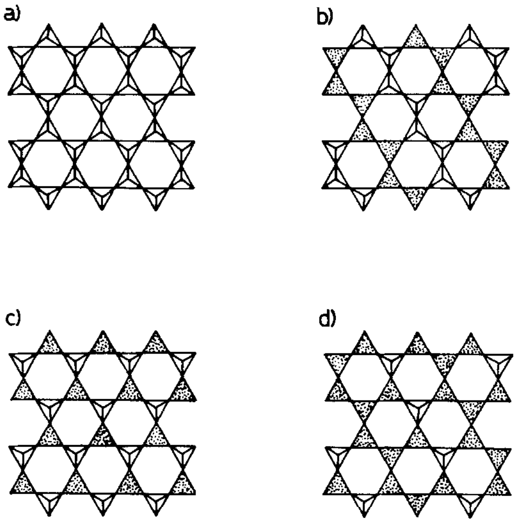

FIG. 2. The four different orientations of the apices (As atoms) of AsO_3 pyramids in six-membered rings connected to neutral As_2O_3 sheets, which have been determined until now. The topological differences are characterized in idealized figures. (a) $(NH_4Cl \cdot As_2O_3)_2 \cdot H_2O$ (*1*). (b) As_2O_3 (claudetite I) (*7*). (c) As_2O_3 (claudetite II) (*6*). (d) $NaAs_4O_6Br$.

three representatives these sheets are more or less waved; in the last one the As_2O_3 sheet is strictly planar. Figure 2 shows these connections of AsO_3 pyramids to four topologically different As_2O_3 sheets. These sheets consist of six-membered rings formed by the connection of the arsenite groups. In $(NH_4Cl \cdot As_2O_3)_2 \cdot H_2O$ all the As atoms of the As_2O_3 sheet are arranged on the same side in relation to the O atom plane (Fig. 2a). In claudetite I and II half of the As atoms are on different sides of the least-squares plane defined by the O atoms. In claudetite I (Fig. 2b) rows of AsO_3 pyramids with the same orientation are formed within the six-membered ring; in claudetite II (Fig. 2c) the directions of the As apices are alternately oriented in opposite directions. The As_2O_3 sheets in $NaAs_4O_6Br$ (Fig. 2d) contain two kinds of six-membered arsenite rings: (a) all but one and (b) all but two arsenite groups show the same orientation. It is worth mentioning that no further connections of AsO_3 groups to neutral sheets except the shown four types of six-membered rings have been determined before now.

Acknowledgment

This work was supported by the Hochschuljubiläumsstiftung der Stadt Wien.

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