

Preparation and Characterization of AlAsO_4-3 and AlAsO_4-4 , Two New Aluminoarsenates with Occluded 1,2-Diaminopropane

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Two new amine-occluding aluminoarsenates (designated AlAsO_4-3 and AlAsO_4-4) with compositions $\text{AlAsO}_4 \cdot 0.3\text{C}_3\text{H}_{10}\text{N}_2 \cdot 0.2\text{H}_2\text{O}$ and $\text{AlAsO}_4 \cdot 0.2\text{C}_3\text{H}_{10}\text{N}_2 \cdot 0.4\text{H}_2\text{O}$ were prepared hydrothermally by using 1,2-diaminopropane as a template. The former is indexable on the basis of a cubic cell with $a = 7.722 \text{ \AA}$ and the latter, a monoclinic one with $a = 19.255$, $b = 12.013$, $c = 10.356 \text{ \AA}$, and $\beta = 127.58^\circ$. AlAsO_4-3 contains octahedrally coordinated Al atoms whereas AlAsO_4-4 contains not only octahedrally coordinated Al atoms but also tetrahedrally coordinated ones. In Al-O-As bond force, these two compounds are different to a great extent from each other as well as from α -quartz-type AlAsO_4 which contains AlO_4 and AsO_4 coordination units. When calcined at high temperature (e.g., 800°C), both lose the template completely and the framework arsenic partially. © 1990 Academic Press, Inc.

Introduction

In 1982, a new family of aluminophosphates (designated AlPO_4-n) with open frameworks and occluded amines was announced (1). On calcination, these compounds become porous and possess structures and properties similar to those of zeolites (2-4). So far, about 30 varieties of such aluminophosphates have been synthe-

sized and the family has been expanding constantly (5, 6). As to aluminoarsenates with Al/As = 1, the well-known ones are the dense AlAsO_4 polymorphs (7, 8) and the $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$ (9) with variscite structure. Earlier, we reported two novel aluminoarsenates (denoted as AlAsO_4-1 and AlAsO_4-2 , respectively) with occluded ethanolamine (10) and tetramethylammonium hydroxide (11). The structure of AlAsO_4-1 is related to APD (12) and can be described by net 622 of Smith (13).

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To extend the family of AlAsO_4-n , we have tried to synthesize amine-occluding aluminarsenates using various amines as templates. This article will present the preparation of two new aluminarsenates with occluded 1,2-diaminopropane (designated AlAsO_4-3 and AlAsO_4-4 , respectively), their characterization based on X-ray powder diffraction, MAS NMR (magic angle spinning nuclear magnetic resonance) and IR spectrometries, and their thermal properties.

Experimental

Preparation of AlAsO_4-3 . Aluminum isopropoxide, pyroarsenic acid, template 1,2-diaminopropane (DAP), and water were mixed in a mole ratio of 1.0 Al_2O_3 :1.4 As_2O_5 :0.7 DAP:40 H_2O . The reaction mixture was stirred until homogeneous, then sealed in a Teflon-lined autoclave and heated at 200°C for 5 days. The product was filtered, washed with water, and dried at ambient temperature.

Preparation of AlAsO_4-4 . The procedure was the same as for AlAsO_4-3 except that the mole ratio adopted was 1.0 Al_2O_3 :1.5 As_2O_5 :1.0 DAP:40 H_2O .

The SEM (scanning electronic micrographs) were taken with a Hitachi X-650 SEM instrument. The X-ray powder diffraction data were recorded on a Rigaku D/MAX IIIA diffractometer by using $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) for radiation and silicon as external standard. The elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer; IR spectra, on a Nicolet 5DX IR spectrometer; and DTA-TG, on a Rigaku thermobalance.

The ^{27}Al MAS NMR measurements were carried out on a Bruker MSL-400 NMR spectrometer with a magnetic field strength of 9.4 T. The spinning rates were 5 kHz and the spectra were obtained at 104.3 MHz. The single pulse excitation (no high power decoupling) technique was used and the ac-

quisition parameters adopted were: pulse width, 6.5 μsec ; recycle delay, 1 sec; number of acquisition, 500; acquisition time, 10 msec. The line broadening factors were 20 Hz. The chemical shifts obtained were relative to external $\text{Al}(\text{H}_2\text{O})_6^{3+}$. Incomplete removal of second-order quadrupole effects were suggested by the small spinning side bands (asterisks in Fig. 2).

Results and Discussion

AlAsO_4-3 appears to be cubic-shaped and AlAsO_4-4 , rhombic-plate-shaped (Fig. 1). One can see from the graphs that the latter is much larger in size than the former. To obtain pure phases of both, the reaction conditions had to be controlled carefully. In general, AlAsO_4-3 and AlAsO_4-4 crystallized simultaneously, and the larger the value of $\text{As}_2\text{O}_5/(\text{Al}_2\text{O}_3 + \text{DAP})$, the more the former was contained in the reaction product. It is of interest that for AlAsO_4-3 , after a certain period (e.g., 5 months) a structural change from tetragonal form to cubic one occurred on the basis of the X-ray powder diffraction data; on the other hand, nothing happened to AlAsO_4-4 with time. This phenomenon is under further investigation. In this article the characterization involved is referred to the AlAsO_4-3 with cubic lattice symmetry.

Chemical and elemental analyses gave a composition of $\text{AlAsO}_4 \cdot 0.3\text{C}_3\text{H}_{10}\text{N}_2 \cdot 0.2\text{H}_2\text{O}$ for AlAsO_4-3 and one of $\text{AlAsO}_4 \cdot 0.2\text{C}_3\text{H}_{10}\text{N}_2 \cdot 0.4\text{H}_2\text{O}$ for AlAsO_4-4 . The X-ray powder diffraction data, which showed that both AlAsO_4-3 and AlAsO_4-4 are of new structure, were indexed with the TREOR program (14). The indexed results suggest that the crystal lattice of AlAsO_4-3 has cubic symmetry with cell dimension $a = 7.722 \text{ \AA}$ whereas that of AlAsO_4-4 is monoclinic with cell parameters $a = 19.255$, $b = 12.013$, $c = 10.356 \text{ \AA}$ and $\beta = 127.58^\circ$. All the observed and calculated interplanar d -

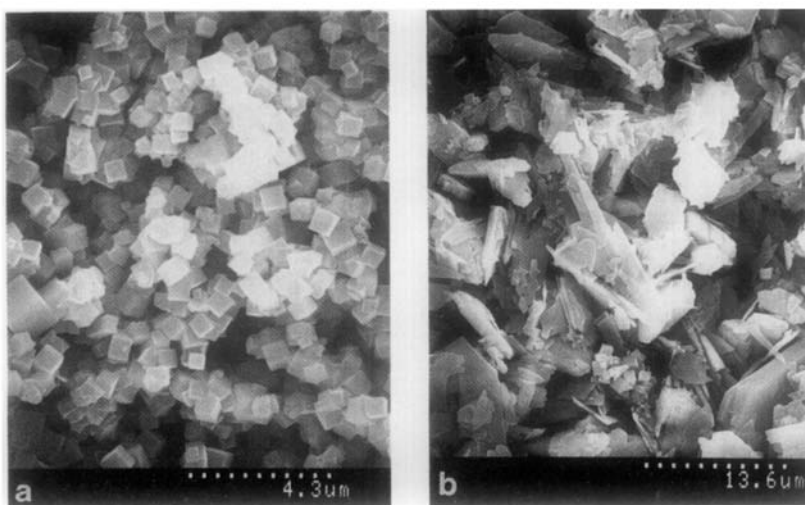


Fig. 1. Scanning electronic micrographs of (a) AlAsO₄-3 and (b) AlAsO₄-4.

spacings, and the Miller indices are presented in Tables I and II, respectively.

Figure 2 shows the experimental ²⁷Al MAS NMR spectra of AlAsO₄-1 (10), AlAsO₄-3, and AlAsO₄-4. The corresponding data are listed in Table III. A single crystal structural analysis showed (10) that AlAsO₄-1 contained two types of Al atoms. One type each was tetrahedrally coordinated and the other each was octahedrally coordinated by oxygen atoms. Several other papers (15-17) described that for open framework aluminophosphates with occluded amines, tetrahedrally coordinated Al atoms gave MAS NMR signals at chemical shifts between 20 and 50 ppm and octahedrally coordinated Al atoms gave ones at chemical shifts around or below 0 ppm. That is, the chemical shifts of AlO₄ units are always higher than those of AlO₆ units. This rule is expected to be applicable to other types of compounds considering that the Al in an AlO₄ unit is less shielded than that in an AlO₆ unit (18). In Fig. 2, AlAsO₄-1 exhibits two signals with maxima at 41.4 and 1.7 ppm, respectively. The former value is close to that of α-quartz type AlAsO₄ (19) containing only AlO₄ coordination units.

Without doubt, the signal of AlAsO₄-1 at 41.4 ppm corresponds to the tetrahedrally coordinated Al atoms and that of it at 1.7 ppm to the octahedrally coordinated ones.

For AlAsO₄-3, the ²⁷Al NMR spectrum shows a single peak with maximum at chemical shift 0.1 ppm, very close to the value of the higher-field signal of AlAsO₄-1. This reveals that the Al atoms in AlAsO₄-3 are octahedrally coordinated. In contrast, AlAsO₄-4 gives two ²⁷Al NMR signals with

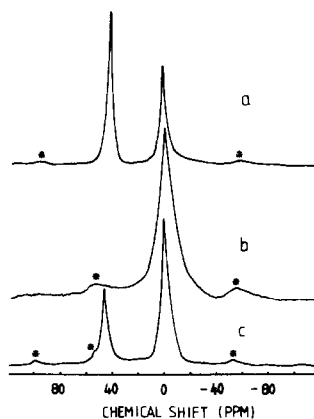


Fig. 2. ²⁷Al MAS NMR spectra of (a) AlAsO₄-1, (b) AlAsO₄-3, and (c) AlAsO₄-4.

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR AlAsO_4-3

I_{obsd}	d_{obsd} (Å)	d_{calcd} (Å)	$h k l$
vs	7.725	7.722	1 0 0
s	4.466	4.458	1 1 1
m	3.8664	3.8611	2 0 0
vw	3.4534	3.4535	2 1 0
m	3.1533	3.1526	2 1 1
m	2.7295	2.7302	2 2 0
vw	2.5750	2.5740	3 0 0/2 2 1
w	2.4428	2.4419	3 1 0
w	2.3288	2.3283	3 1 1
vw	2.2295	2.2291	2 2 2
vvw	2.1402	2.1417	3 2 0
vvw	2.0645	2.0638	3 2 1
vvw	1.9306	1.9305	4 0 0
vvw	1.8725	1.8729	4 1 0/3 2 2
vvw	1.8200	1.8201	4 1 1/3 3 0
vw	1.7716	1.7716	3 3 1
vw	1.7267	1.7267	4 2 0
vvw	1.6844	1.6851	4 2 1
vvw	1.6465	1.6464	3 3 2
vw	1.5767	1.5763	4 2 2
vw	1.5446	1.5446	5 0 0/4 3 0
vvw	1.5139	1.5144	5 1 0/4 3 1
vw	1.4858	1.4861	5 1 1/3 3 3
vvw	1.4102	1.4099	5 2 1
vw	1.3648	1.3651	4 4 0
vvw	1.3441	1.3443	5 2 2/4 4 1
vw	1.3055	1.3053	5 3 1
vvw	1.2875	1.2870	6 0 0/4 4 2
vvw	1.2207	1.2210	6 2 0
vvw	1.2059	1.2060	6 2 1/5 4 0
vvw	1.1777	1.1776	5 3 3
vvw	1.1641	1.1642	6 2 2

maxima at 45.9 and 0.1 ppm, respectively. The former is even 4.5 ppm larger than the lower-field chemical shift value of AlAsO_4-1 , whereas the latter is just the same as the chemical shift value of AlAsO_4-3 . It is reasonable that AlAsO_4-4 contains both tetrahedrally coordinated Al atoms and octahedrally coordinated Al atoms. As in several AlPO_4-n (20–22), the two extra coordinating oxygen atoms of the AlO_6 units in AlAsO_4-4 as well as in AlAsO_4-3 may be attributed to OH groups which result from

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR AlAsO_4-4

I_{obsd}	d_{obsd} (Å)	d_{calcd} (Å)	$h k l$
vs	10.327	10.314	$\bar{1}$ 0 1
vw	5.276	5.284	$\bar{1}$ 1 1
vw	5.152	5.157	$\bar{2}$ 0 2
vw	4.756	4.756	$\bar{1}$ 0 2
		4.739	$\bar{2}$ 1 2
w	4.186	4.185	4 1 2
w	4.110	4.104	0 0 2
vw	3.8792	3.8815	3 2 0
vw	3.8548	3.8543	$\bar{3}$ 2 2
vw	3.6360	3.6358	4 1 0
w	3.4422	3.4378	$\bar{3}$ 0 3
vvw	3.1441	3.1463	$\bar{3}$ 3 0
		3.1430	$\bar{5}$ 2 1
vvw	3.0311	3.0330	$\bar{1}$ 0 3
vvw	2.8306	2.8304	$\bar{6}$ 2 2
vvw	2.7204	2.7208	5 2 0
		2.7202	$\bar{3}$ 4 1
vvw	2.4943	2.4919	4 4 2
		2.4909	$\bar{7}$ 2 2
vvw	2.4588	2.4594	$\bar{6}$ 1 4
vvw	2.3651	2.3693	$\bar{4}$ 2 4
		2.3676	$\bar{8}$ 0 2
vvw	2.3218	2.3229	$\bar{8}$ 1 2
		2.3201	$\bar{2}$ 5 1
vvw	2.0646	2.0636	6 1 1
		2.0627	$\bar{5}$ 0 5
vvw	1.7225	1.7220	8 3 0

the transfer of protons from the occluded H_2O molecules to the template molecules.

Table IV presents the frequencies of the main IR absorptions of zeolite NaY, zeolite ZSM-5 with occluded tetramethylam-

TABLE III

 ^{27}Al MAS NMR DATA FOR AlAsO_4-1 , AlAsO_4-3 , AND AlAsO_4-4

AlAsO_4-n	Chemical shift (ppm)	Half width (Hz)
1	41.4, 1.7	380, 600
3	0.1	1360
4	45.9, 0.1	630, 830

TABLE IV

FREQUENCIES OF THE MAIN IR ABSORPTIONS OF NaY, ZSM-5, α -AlPO₄, AlPO₄-5, α -AlAsO₄, AlAsO₄-1, AlAsO₄-3, and AlAsO₄-4

Material	Frequency (cm ⁻¹)	Ref.
Zeolite NaY	985	(23)
Zeolite ZSM-5	1100	(24)
α -AlPO ₄	1124	This work
AlPO ₄ -5	1125	(28)
α -AlAsO ₄	945	(7)
AlAsO ₄ -1 ^a	962, 871, 920	This work
AlAsO ₄ -3	857	This work
AlAsO ₄ -4 ^a	779, 963, 920	This work

^a The frequencies are in order of intensity.

monium, α -AlPO₄, AlPO₄-5 with occluded triethylamine, α -AlAsO₄, AlAsO₄-1, AlAsO₄-3, and AlAsO₄-4. The corresponding IR spectra of AlAsO₄-3 and AlAsO₄-4 within 4000 to 400 cm⁻¹ are shown in Fig. 3. According to Flanigen *et al.*, the main IR absorptions (1200–950 cm⁻¹) of zeolites with open frameworks composed of SiO₄ and AlO₄ units are always assigned to the T–O (T = Si and Al without distinguishing between them) asymmetric stretch vibrations (23–25). In general, with increase of the Si/Al ratio in the framework, the main IR absorption shifts toward higher frequency. The main IR absorptions of α -quartz type AlPO₄ (26, 27) and AlPO₄-5 (28) around 1120 cm⁻¹ are also assigned to the T–O (T = Al and P) asymmetric stretch vibrations without distinguishing between the Al and the P atoms. In addition, the removal of the occluded templates has no influence on the main IR absorptions both for the ZSM-5 and the AlPO₄-5, revealing that the templates do not contribute to the main IR absorptions of these compounds.

It is expected that the T–O vibrational absorptions of aluminarsenates should shift toward lower frequencies compared with the corresponding absorptions of aluminophosphates because of the larger mass of

As relative to that of P. In fact, α -quartz type AlAsO₄ shows (7) a strong IR vibrational band with maximum at 945 cm⁻¹, almost 200 cm⁻¹ lower than the corresponding vibrational frequencies for α -AlPO₄ and AlPO₄-5. The strongest IR absorption of AlAsO₄-3 is at 857 cm⁻¹, even 88 cm⁻¹ lower than that of α -AlAsO₄. Similarly, we assign the absorption to the T–O (T = Al and As) asymmetric stretch vibration neglecting the influence of the occluded template as for ZSM-5 and AlPO₄-5. The relatively lower vibrational frequency suggests that the Al–O–As bond force in AlAsO₄-3 is weaker than that in α -AlAsO₄. This result may be related to the octahedrally coordinated Al atoms in the former. AlAsO₄-4 has an extremely different whereas much more complicated IR spectrum. The strongest absorption band appears at 779 cm⁻¹, meanwhile, there are another two strong absorptions with intensities next to the strongest one at 963 and 920 cm⁻¹, respectively. Since there is no strong absorption around these frequencies in the corresponding spectrum of AlAsO₄-3 whose template is the same as that of AlAsO₄-4, all the three absorptions for AlAsO₄-4 must be attributed to the framework of AlAsO₄-4 rather than

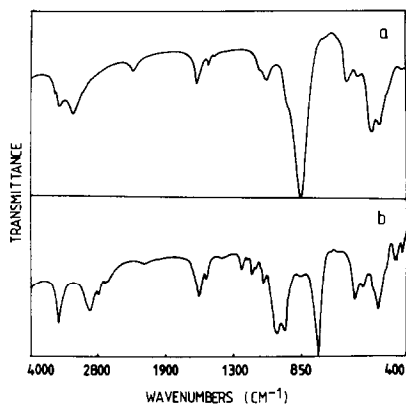


FIG. 3. IR spectra of (a) AlAsO₄-3 and (b) AlAsO₄-4.

the template it occludes. The first is 166 cm^{-1} lower in frequency than the strong absorption of $\alpha\text{-AlAsO}_4$. The second and the third absorptions are close to the higher-frequency absorptions of AlAsO_4-1 as well as the strong absorption of $\alpha\text{-AlAsO}_4$. Consequently, we conclude that AlAsO_4-4 may contain Al-O-As with bond force as strong as $\alpha\text{-AlAsO}_4$ and that with bond force even weaker than AlAsO_4-3 . Further assignment of the absorptions is difficult.

To investigate the thermal properties of AlAsO_4-3 and AlAsO_4-4 , DTA-TG analyses in N_2 atmosphere were carried out and the curves are shown in Fig. 4. For AlAsO_4-3 , there exists an endothermic effect near 360°C and two exothermic ones around 507 and 790°C , respectively. The TG curve can be divided into two stages ranging from 300 to 650°C and 650 to 800°C . The corresponding weight losses are 20.7 and 21.9% , respectively with a total of 42.6% . Apparently, some amount of framework atoms escaped from the solid after calcination at high temperature since the content of the template and water did not exceed 15% in AlAsO_4-3 . The chemical analysis showed that the As/Al ratio in the calcination residual of AlAsO_4-3 was

as low as 0.3 , revealing that it was arsenic that escaped from the solid at high temperature. Furthermore, the major components of the gas produced within $300\text{--}400^\circ\text{C}$ were confirmed by mass spectroscopy to be water and decomposition products of 1,2-diaminopropane. This suggests that the thermal effect around 360°C should be mainly attributed to the sublimation of the occluded water and the pyrolysis of the template. The exothermic effect around 507°C may be due to the oxidation-reduction of the framework As(V) and the template, and that around 790°C to a phase transition of the solid since there is no distinct weight loss observed corresponding to the effect. After calcination at 400°C , AlAsO_4-3 becomes amorphous in terms of the X-ray powder diffraction pattern, indicating this compound is not as stable as most AlPO_4-n . AlAsO_4-4 shows three distinct endothermic DTA effects with peak maxima at 271 , 361 , and 625°C , respectively. The mass spectroscopy proves that the first is exclusively attributed to water loss and the second to both template pyrolysis and water loss. This result implies the presence of two types of water molecules in AlAsO_4-4 , one being bonded loosely and the other being bonded tightly. The third effect, that around 625°C , may be assigned to a dramatic loss of the framework arsenic since at such high temperature template molecules should not remain for pyrolysis. At every temperature around which thermal effect appears, evident weight loss is observed on the TG curve. In addition, there is a pronounced weight loss around 800°C without observable thermal effect. The total weight loss for AlAsO_4-4 is about 37.8% , less than that of AlAsO_4-3 but also suggests the sublimation of framework arsenic from the solid because the content of the template and water is only about 12% according to the composition. The As/Al ratio in the calcination residual of AlAsO_4-4 is about 0.5 ,

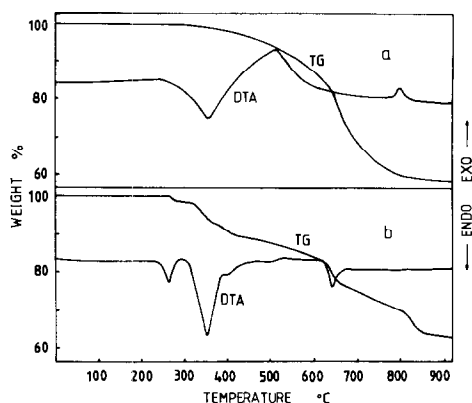


FIG. 4. DTA-TG curves in N_2 atmosphere of (a) AlAsO_4-3 and (b) AlAsO_4-4 . Temperature rate = $10^\circ\text{C}/\text{min}$ and N_2 stream speed = $50\text{ ml}/\text{min}$.

well comparable to the value for AlAsO_4-3 . Differing from that of AlAsO_4-3 , the DTA curve of AlAsO_4-4 shows no distinct exothermic effect, suggesting that the reaction of As(V)-template is not dramatic. It is also indicated by X-ray powder diffraction that calcined at 400°C , AlAsO_4-4 changes from crystalline form to amorphous form.

In summary, the successful preparation of the third and fourth amine-occluding aluminoarsenates illustrates that as the AlPO_4-n family, the AlAsO_4-n family may be extended to include a large number of members. Generally, AlAsO_4-n contain octahedrally coordinated Al atoms. Some of them contain both octahedrally and tetrahedrally coordinated Al atoms. Unlike AlPO_4-n , AlAsO_4-n are unstable at higher temperature. With the increase of the calcination temperature, the framework arsenic as well as the template occluded volatilize from the solid, revealing that AlAsO_4-n are not suitable to be used as molecular sieves as AlPO_4-n are.

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