# Synthesis and Characterization of Two Aluminoarsenates with Occluded Ethylenediamine

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Two framework aluminoarsenates (designated $AlAsO_4$-5 and $AlAsO_4$-6 respectively) were synthesized hydrothermally in the presence of a template ethylenediamine by varying the composition of the reaction mixture. The compound $AlAsO_4$-5 is indexable on the basis of a monoclinic structure with $a$ = 11.777, $b$ = 18.960, $c$ = 5.981 Å and β = 94.85°. The structure of $AlAsO_4$-6 is also monoclinic but $a$ = 19.953, $b$ = 6.636, $c$ = 10.604 Å and β = 96.88°. Both compounds contain six-co-ordinated Al and the extra two ligands, that is those other than the four O atoms bridging between alternating Al and As, are believed to be hydroxyl groups. In contrast to most framework aluminophosphates, $AlAsO_4$-5 and $AlAsO_4$-6 have poor thermal stability. Calcination at elevated temperature results in not only the collapse of the framework structure but also the sublimation of As from the solid phases.

Since 1982 a large number of crystalline framework aluminophosphates (designated $AlPO_4$-*n* with *n* representing various structures) have been synthesized from aluminophosphate gels containing various amines and quaternary ammoniums.[1–3] On calcination at elevated temperature the majority become microporous without structural destruction. As a result, like zeolites, they have the potential to act as adsorbents and catalysts and can be viewed as molecular sieves. Structurally, most $AlPO_4$-*n* are exclusively composed of $PO_4$ and $AlO_4$ primary building units; a few contain $AlO_5$ even $AlO_6$ units.[4,5] In 1985 a series of framework gallophosphates was announced.[6] Since then much attention has been attracted to the new family.[7–9] Several framework gallophosphates are isostructural with $AlPO_4$-*n* and are designated in the same way, while others are designated optionally. Quite a number of $AlPO_4$-*n* as well as $GaPO_4$-*n* can be formed by using various templates and, in turn, some templates can lead to the formation of various framework structures. The template ethylenediamine is able to direct the crystallization of $AlPO_4$-12, $AlPO_4$-21, and $AlPO_4$-EN3 in aluminophosphate gels,[10] and that of $GaPO_4$-12,[11] $GaPO_4$-21,[12] and an unnumbered framework $GaPO_4$[6] in gallophosphate gels. In all these ethylenediamine-occluding compounds the P atoms are invariably four-co-ordinated whereas the Al(Ga) atoms are either four- or five-co-ordinated by O atoms. The extra O atoms of an $AlO_5$ unit belong to a hydroxyl group which is necessary to balance the positive charge of the protonated ethylenediamine occluded. Recently, we have reported several novel aluminoarsenates with an occluded amine or quaternary ammonium.[13–16] They were synthesized similarly to $AlPO_4$-*n* and $GaPO_4$-*n*. It is interesting to determine whether framework aluminoarsenates can crystallize in the presence of ethylenediamine, and if so what are the features of their frameworks. This article presents the synthesis and characterization of two ethylenediamine-occluding aluminoarsenates, designated $AlAsO_4$-5 and $AlAsO_4$-6 respectively, according to our experimental sequence.

## Experimental

The preparation was carried out as follows. Aluminium isoproxide, diarsenic acid, ethylenediamine (en), and water were mixed in molar proportions $Al_2O_3$:$x$$As_2O_5$:$y$en:$40H_2O$, where $x$ = 1.0—1.5 and $y$ = 0.4—1.4. The reaction mixture was carefully stirred to give a homogeneous gel, sealed in Teflon-lined stainless-steel bombs, and heated at 200 °C for 5 d. The bombs were quenched to room temperature with water and the products were treated, if containing amorphous gel, ultrasonically, filtered, washed with distilled water, and dried in air at ambient temperature.

Elemental analysis was performed on a Perkin-Elmer 240C element analyser. *X*-Ray powder diffraction data were obtained by using a Rigaku D/MAX diffractometer with Cu-$K_\alpha$ radiation (λ = 1.5418 Å). Silicon powder was used as an external standard to verify the measured lines. All samples were ground to a fine powder and scanned from 4 to 80° (2θ), the scan speed being 0.4° $min^{-1}$. The line intensities were estimated visually. The i.r. measurements were carried out on a Nicolet 5DX FTIR spectrometer utilizing KBr pellets. Aluminium-27 magic angle spinning (m.a.s.) n.m.r. spectra were recorded on a Varian XL-200 spectrometer with a magnetic field strength of 4.7 T. The spinning rates were about 3 kHz. The single-pulse excitation technique was applied and the spectra were obtained at 52.1 MHz. Other parameters adopted were: pulse width, 6 μs; recycle delay, 0.7 s; number of transients, 1 000. The chemical shifts were relative to the external standard $[Al(H_2O)_6]^{3+}$. Carbon-13 m.a.s. n.m.r. spectra were measured on a Bruker MSL-400 spectrometer (9.4 T). The spinning rates were also 3 kHz. The cross-polarization technique was applied, at 100.6 MHz. The contact time was 5.0 ms and the scan number 1 000 with a recycle delay of 2 s. The chemical shifts were relative to $SiMe_4$.

A Rigaku thermobalance was used to obtain the differential thermal analysis (d.t.a.) and thermogravimetric analysis (t.g.a.) curves both in $N_2$ and in air. The heating rate was 10 °C $min^{-1}$ and the flow of either $N_2$ or air was 50 $cm^3$ $min^{-1}$. Since arsenic is destructive of platinum crucibles, carefully processed $Al_2O_3$ cells were used.

## Results and Discussion

*Formation and Compositions of* $AlAsO_4$-5 *and* $AlAsO_4$-6.—By varying the composition of the reaction mixture, $AlAsO_4$-5 and $AlAsO_4$-6 can both be obtained from the system containing aluminoarsenate gel and ethylenediamine. Details of the reaction ratios and the products obtained at 200 °C are presented in Table 1. We have also attempted the synthesis at 150 and 230 °C respectively, nevertheless it was found that at the former a large quantity of unreacted gel remained in the product whereas at the latter the template ethylenediamine was readily oxidized by the $As^V$. As a result, only 200 °C was selected as the crystallization temperature. In general, $AlAsO_4$-5 and $AlAsO_4$-6 crystallized simultaneously. The formation of $AlAsO_4$-5 was favoured by high $As_2O_5/Al_2O_3$ and low en/$Al_2O_3$ ratios. However, if the two ratios each exceeded its own limit, either oxidation of the en molecules by $As^V$ or formation of en-free aluminoarsenate occurred. On the contrary, $AlAsO_4$-6 crystallized preferably under at low $As_2O_5/Al_2O_3$ and high en/$Al_2O_3$ ratios. That is, to avoid the coexistence of the two framework aluminoarsenates in the product, the basicity of the reaction mixture for $AlAsO_4$-6 should be as high as possible. On the other hand, without $AlAsO_4$-5 in the product, $AlAsO_4$-6 was invariably accompanied by unreacted amorphous gel, which could be removed ultrasonically.

**Table 1.** Reaction ratios and products for the $Al_2O_3$–$As_2O_5$–en–$H_2O$ system

| $As_2O_5/Al_2O_3$ | en/$Al_2O_3$ | Product[a] |
|---|---|---|
| 1.0 | 0.40 | $AlAsO_4$-5 + A |
| 1.0 | 0.60 | $AlAsO_4$-5 + $AlAsO_4$-6 |
| 1.0 | 0.80 | $AlAsO_4$-6 + gel |
| 1.0 | 1.00 | $AlAsO_4$-6 + gel |
| 1.25 | 0.60 | $AlAsO_4$-5 + A |
| 1.25 | 0.80 | $AlAsO_4$-5 |
| 1.25 | 1.00 | $AlAsO_4$-6[b] |
| 1.25 | 1.20 | $AlAsO_4$-6 + gel |
| 1.5 | 0.80 | $AlAsO_4$-5 |
| 1.5 | 1.00 | $AlAsO_4$-5 + $AlAsO_4$-6 |
| 1.5 | 1.20 | $AlAsO_4$-5 + $AlAsO_4$-6 |
| 1.5 | 1.40 | $AlAsO_4$-6 + gel |

[a] A represents a variscite-type aluminoarsenate hydrate. [b] $AlAsO_4$-6 was inevitably accompanied by unreacted gel and the lower the basicity of the system the less was the gel amount in the product.

Under an optical microscope $AlAsO_4$-5 appeared as needles and $AlAsO_4$-6 as thin plates. Both chemical and *X*-ray fluorescence analyses gave an As/Al ratio of about 1.0:1 for either $AlAsO_4$-5 or $AlAsO_4$-6, indicating that as for every reported framework aluminophosphate the frameworks of the two aluminoarsenates were neutral. Elemental analysis demonstrated that $AlAsO_4$-5 contained 4.70% C, 2.30% H, and 5.65% N with C:H:N = 1:5.89:1.04. The corresponding C:H:N ratio of ethylenediamine, which is believed to act as a template in the preparation, is 1:4:1. The disagreement between the two ratios is attributable to the presence of water molecules in $AlAsO_4$-5. The empirical composition calculated on the basis of the data given above is $AlAsO_4 \cdot 0.41en \cdot 0.76H_2O$, which can be normalized to $5AlAsO_4 \cdot 2en \cdot 4H_2O$. The C, H, N contents of $AlAsO_4$-6 are 4.80, 2.20, and 5.55% respectively with C:H:N = 1:5.49:1. Accordingly, the calculated empirical composition for $AlAsO_4$-6 is $AlAsO_4 \cdot 0.40en \cdot 0.60H_2O$ corresponding to an idealized formula of $5AlAsO_4 \cdot 2en \cdot 3H_2O$.

*X-Ray Powder Diffraction.*—The *X*-ray powder diffraction data and their indexing results obtained with the TREOR program[17] show that both $AlAsO_4$-5 and $AlAsO_4$-6 have a unique structure. The *d* spacings and indices of the two compounds are listed in Tables 2 and 3 respectively. The cell parameters indexed for $AlAsO_4$-5 are $a$ = 11.777, $b$ = 18.960, $c$ = 5.981 Å and $\beta$ = 94.85°. For $AlAsO_4$-6 the unit cell indexed is also monoclinic with the parameters $a$ = 19.953, $b$ = 6.636, $c$ = 10.604 Å and $\beta$ = 96.88°. It is difficult to ascertain the space groups of the two compounds only on the basis of the systematic absences of the diffraction lines.

*I.r. Spectra.*—Figure 1 shows the i.r. spectra of $AlAsO_4$-5 and $AlAsO_4$-6. The two compounds have quite different vibrational absorptions especially within the lower-frequency range where the absorptions are related to the frameworks,[18,19] although their compositions are similar. This result indicates that the Al–O–As bond in $AlAsO_4$-5 differs to a certain degree from that in $AlAsO_4$-6. Both spectra exhibit relatively strong absorptions around 3 500 cm$^{-1}$, revealing the presence of OH groups in the two aluminoarsenates. The doublet for $AlAsO_4$-5 suggests that there may be two types of OH groups with one having stronger

**Table 2.** Observed and calculated *X*-ray powder diffraction data for $AlAsO_4$-5

| $d_{obs.}$ (Å) | $d_{calc.}$ (Å) | $(I/I_0)_{obs.}$ | *h* | *k* | *l* |
|---|---|---|---|---|---|
| 9.477 | 9.480 | 100 | 0 | 2 | 0 |
| 5.613 | 5.605 | 2 | 2 | 1 | 0 |
| 5.489 | 5.505 | 4 | −1 | 0 | 1 |
| 5.029 | 5.046 | 4 | 0 | 2 | 1 |
| 4.741 | 4.740 | 2 | 0 | 4 | 0 |
| 4.374 | 4.370 | 5 | −2 | 0 | 1 |
| 4.302 | 4.300 | 2 | 2 | 3 | 0 |
| 3.992 | 3.988 | 4 | 1 | 3 | 1 |
| 3.688 | 3.687 | 2 | 2 | 4 | 0 |
| 3.407 | 3.405 | 47 | −3 | 0 | 1 |
| 3.159 | 3.160 | 15 | 0 | 6 | 0 |
| 3.110 | 3.108 | 4 | 3 | 1 | 1 |
| 2.9884 | 2.9896 | 7 | 3 | 2 | 1 |
|  | 2.9800 |  | 0 | 0 | 2 |
| 2.9302 | 2.9338 | 2 | 4 | 0 | 0 |
| 2.6928 | 2.6953 | 12 | 0 | 3 | 2 |
|  | 2.6922 |  | 1 | 6 | 1 |
| 2.5212 | 2.5236 | 5 | −2 | 3 | 2 |
|  | 2.5228 |  | 0 | 4 | 2 |
| 2.4947 | 2.4946 | 5 | 4 | 4 | 0 |
| 2.4540 | 2.4527 | 4 | −3 | 1 | 2 |
| 2.3698 | 2.3700 | 4 | 0 | 8 | 0 |
| 2.3217 | 2.3231 | 2 | 1 | 8 | 0 |
|  | 2.3204 |  | 4 | 5 | 0 |
| 2.2609 | 2.2631 | 3 | 3 | 1 | 2 |
|  | 2.2597 |  | 2 | 4 | 2 |
| 2.1052 | 2.1033 | 4 | 5 | 4 | 0 |
| 2.0327 | 2.0324 | 1 | −5 | 4 | 1 |
| 1.8970 | 1.8977 | 5 | −2 | 9 | 1 |
|  | 1.8972 |  | −6 | 1 | 1 |
|  | 1.8960 |  | 0 | 10 | 0 |
| 1.8007 | 1.8017 | 5 | 2 | 2 | 3 |
|  | 1.8016 |  | −3 | 2 | 3 |
| 1.5802 | 1.5805 | 5 | 7 | 4 | 0 |
|  | 1.5800 |  | 0 | 12 | 0 |
|  | 1.5794 |  | 7 | 0 | 1 |
| 1.5134 | 1.5135 | 4 | −7 | 5 | 1 |
| 1.4414 | 1.4414 | 2 | −6 | 7 | 2 |
| 1.4071 | 1.4077 | 1 | −2 | 4 | 4 |
|  | 1.4071 |  | 7 | 1 | 2 |
| 1.3978 | 1.3978 | 1 | −3 | 3 | 4 |
|  | 1.3977 |  | 1 | 4 | 4 |
| 1.3835 | 1.3837 | 2 | 2 | 9 | 3 |
|  | 1.3835 |  | −2 | 13 | 1 |
| 1.3583 | 1.3590 | 5 | −8 | 1 | 2 |
| 1.3461 | 1.3461 | 5 | 2 | 12 | 2 |

**Table 3.** Observed and calculated *X*-ray powder diffraction data for $AlAsO_4$-6

| $d_{obs.}$ (Å) | $d_{calc.}$ (Å) | $(I/I_0)_{obs.}$ | $h$ | $k$ | $l$ |
|---|---|---|---|---|---|
| 9.899 | 9.905 | 100 | 2 | 0 | 0 |
| 7.681 | 7.688 | 18 | −2 | 0 | 1 |
| 4.939 | 4.952 | 15 | 4 | 0 | 0 |
| | 4.943 | | 1 | 0 | 2 |
| 4.755 | 4.755 | 4 | 2 | 1 | 1 |
| 4.439 | 4.434 | 11 | 2 | 0 | 2 |
| 4.279 | 4.288 | 7 | 4 | 0 | 1 |
| 3.850 | 3.844 | 12 | −4 | 0 | 2 |
| 3.432 | 3.440 | 9 | −2 | 0 | 3 |
| 3.300 | 3.302 | 18 | 6 | 0 | 0 |
| 3.143 | 3.144 | 7 | 5 | 1 | 1 |
| | 3.143 | | −1 | 2 | 1 |
| 2.7207 | 2.7140 | 12 | 4 | 0 | 3 |
| 2.6968 | 2.7000 | 7 | 3 | 1 | 3 |
| 2.6427 | 2.6448 | 4 | −3 | 2 | 2 |
| 2.5693 | 2.5692 | 2 | 1 | 0 | 4 |
| 2.4787 | 2.4774 | 1 | −8 | 0 | 1 |
| | 2.4761 | | 8 | 0 | 0 |
| 2.4384 | 2.4393 | 4 | −2 | 1 | 4 |
| 2.3464 | 2.3485 | 3 | 8 | 0 | 1 |
| | 2.3443 | | −7 | 0 | 3 |
| 2.3231 | 2.3268 | 7 | 6 | 2 | 1 |
| | 2.3260 | | 5 | 1 | 3 |
| | 2.3243 | | −5 | 0 | 4 |
| 2.2241 | 2.2244 | 5 | 5 | 2 | 2 |
| 2.1910 | 2.1937 | 2 | −5 | 1 | 4 |
| | 2.1898 | | −6 | 0 | 4 |
| 2.0596 | 2.0621 | 1 | 0 | 2 | 4 |
| | 2.0597 | | −7 | 2 | 2 |
| | 2.0577 | | −2 | 2 | 4 |
| 1.9811 | 1.9809 | 2 | 10 | 0 | 0 |
| | 1.9794 | | 2 | 3 | 2 |
| 1.9641 | 1.9659 | 2 | 4 | 3 | 1 |
| | 1.9620 | | −7 | 1 | 4 |
| 1.8296 | 1.8314 | 1 | −3 | 3 | 3 |
| | 1.8311 | | −6 | 3 | 1 |
| 1.8180 | 1.8178 | 3 | 2 | 3 | 3 |
| 1.7661 | 1.7665 | 4 | −1 | 0 | 6 |
| | 1.7650 | | 7 | 2 | 3 |
| | 1.7645 | | −2 | 0 | 6 |
| 1.7223 | 1.7236 | 4 | 10 | 1 | 2 |
| 1.6518 | 1.6526 | 2 | 10 | 2 | 1 |
| | 1.6518 | | 5 | 3 | 3 |
| | 1.6509 | | 8 | 1 | 4 |
| 1.6351 | 1.6359 | 1 | −6 | 2 | 5 |
| | 1.6358 | | −1 | 4 | 1 |
| 1.6078 | 1.6091 | 1 | 3 | 4 | 0 |
| | 1.6089 | | −7 | 3 | 3 |
| 1.5104 | 1.5106 | 1 | 1 | 3 | 5 |
| 1.4851 | 1.4852 | 2 | 12 | 1 | 2 |
| | 1.4851 | | 13 | 1 | 0 |
| 1.4328 | 1.4327 | 2 | −6 | 3 | 5 |
| 1.3035 | 1.3033 | 1 | 7 | 2 | 6 |
| | 1.3031 | | 0 | 4 | 5 |

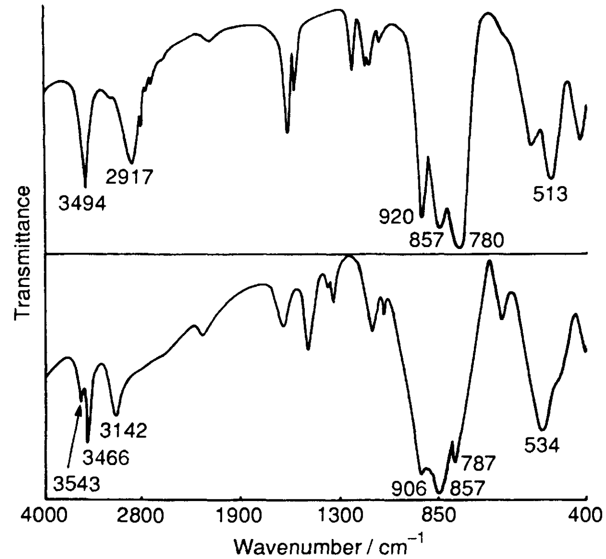

**Figure 1.** I.r. spectra of $AlAsO_4$-5 (bottom) and $AlAsO_4$-6 (top)

O–H bonds than the other. The absorptions around 3 000 cm$^{-1}$ are attributable to the ethylenediamine molecules occluded.

*M.A.S. N.M.R Spectra.*—The compound $AlAsO_4$-5 gave a single $^{13}C$ n.m.r. signal (Figure 2) at 36.1 p.p.m., nearly 9 p.p.m. lower than that (45.0 p.p.m.) of free ethylenediamine and very close to the value (37.6 p.p.m.) of en•2HI or en•$H_2SO_4$.[20] It is reasonable that in $AlAsO_4$-5 the template is protonated. The protons must be from the occluded $H_2O$ molecules since there are no other molecules more prone to dissociate than them in the compound. The compound $AlAsO_4$-6 showed a $^{13}C$ n.m.r. signal essentially the same as that of $AlAsO_4$-5, indicating that the ethylenediamine it occludes is protonated also. Figure 3 shows the $^{27}Al$ m.a.s. n.m.r. spectra of $AlAsO_4$-5 and $AlAsO_4$-6.

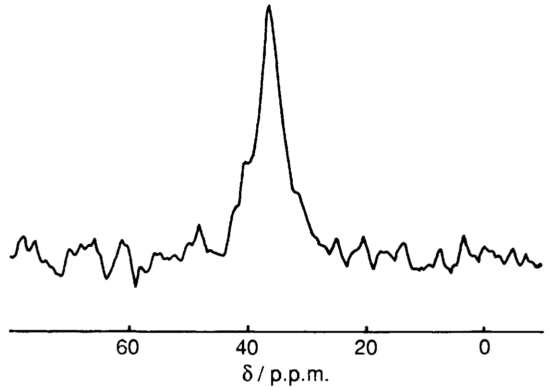

**Figure 2.** $^{13}C$ M.a.s. n.m.r. spectrum of $AlAsO_4$-5

The former has a maximum at −16.5 p.p.m. and the latter one around −8.0 p.p.m. Because of the strong second-order quadruple effects of $^{27}Al$, the two spectra possess considerably large half-widths (1 600 Hz for $AlAsO_4$-5 and 1 300 Hz for $AlAsO_4$-6). We have also recorded the $^{27}Al$ m.a.s. n.m.r. spectrum of $AlAsO_4$-1,[13] which contains both $AlO_4$ and $AlO_6$ units, on the Varian-200 instrument; two signals appeared at 34.5 and −8.1 p.p.m. corresponding to the $AlO_4$ and $AlO_6$ units respectively, in accord with the Al in an $AlO_4$ unit being less shielded than in an $AlO_6$ unit.[21] It was reported[22] that the dense $AlAsO_4$ comprising $AsO_4$ and $AlO_4$ primary building units exhibited a $^{27}Al$ m.a.s. n.m.r. (at 6.2 T) signal at 47.0 p.p.m. The two signals of $AlAsO_4$-5 and $AlAsO_4$-6 are so far away from those for the $AlO_4$ units of $AlAsO_4$-1 as well as dense $AlAsO_4$ that it is impossible for them to be attributed to $AlO_4$ units. On the other hand, their chemical shifts are close to (for $AlAsO_4$-6) or even lower than (for $AlAsO_4$-5) that for the $AlO_6$ unit of $AlAsO_4$-1. Furthermore, some framework aluminophosphates containing $AlO_6$ units also show $^{27}Al$ m.a.s. n.m.r. signals at chemical shifts below zero.[23] All these results lead to the

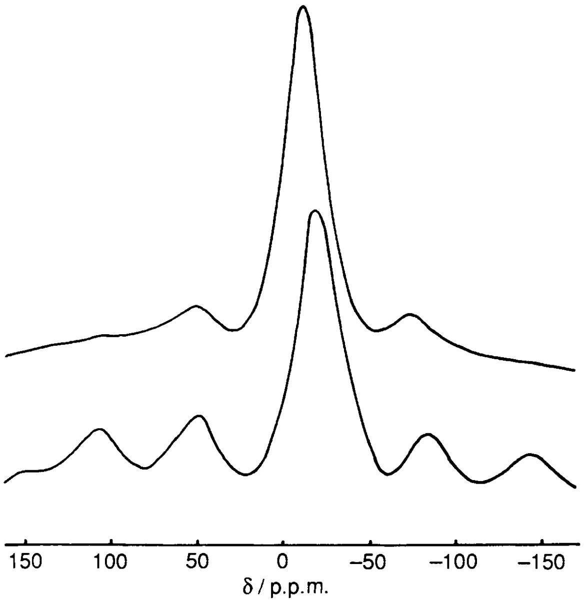

**Figure 3.** $^{27}$Al M.a.s. n.m.r. spectra of $AlAsO_4$-5 (bottom) and $AlAsO_4$-6 (top)

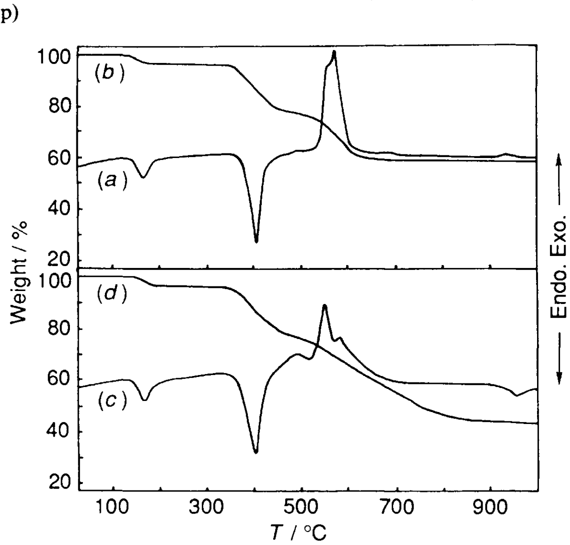

**Figure 4.** D.t.a. [(*a*), (*c*)] and t.g.a. [(*b*), (*d*)] curves for $AlAsO_4$-5 in $N_2$ (bottom) and in air (top)

conclusion that, in contrast to the reported ethylenediamine-occluding alumino- and gallo-phosphates containing both $AlO_4(GaO_4)$ and $AlO_5(GaO_5)$ units, the as-synthesized $AlAsO_4$-5 and $AlAsO_4$-6 contain only six-co-ordinated Al. The extra ligands, that is those other than the four framework O atoms bridging between alternating Al and As, for these six-co-ordinated Al should be hydroxyl groups since as described previously the occluded $H_2O$ molecules are dissociated to provide protons for the ethylenediamine molecules.

*Thermal Properties.*—D.t.a. and t.g.a. analyses were carried out for the two new aluminoarsenates both in $N_2$ and in air. For $AlAsO_4$-5 (Figure 4), in $N_2$ the d.t.a. curve has two distinct endothermic effects at about 172 and 404 °C respectively and a main exothermic effect at 558 °C with a shoulder on the right. The first endothermic effect is attributable to partial loss of the occluded water; its corresponding weight loss reflected by the t.g.a. curve is 3.7%, less than the calculated water content (6.8%) on the basis of the empirical composition. The weight loss corresponding to the second endothermic effect is 15.8%, close to the sum of the calculated template content (12.2%) and the water remaining after the first effect. Therefore, this effect should be mainly assigned to the decomposition of the template as well as another water loss. On calcination at about 400 °C for 2 h, $AlAsO_4$-5 becomes dark and the *X*-ray diffraction pattern indicates that it has transformed into another form of structure, with the crystallinity decreasing considerably. The As/Al ratio of the calcination residue at this temperature remains essentially unchanged. Differing from those of template-occluding zeolites,[24,25] the d.t.a. curve of $AlAsO_4$-5 in $N_2$ exhibits distinct exothermic effects after the decomposition of the template molecules. They must be a reflection of the oxidation-reduction between the $As^V$ and the small quantity of template remaining. The t.g.a. curve shows that the weight loss continues after the template decomposition until about 820 °C, indicating that within this temperature range severe arsenic sublimation occurs. After calcination at about 550 °C for 30 min the solid residue of $AlAsO_4$-5 has an As/Al ratio as low as 0.6 : 1. The total weight loss through the thermal process is about 55%, remarkably exceeding the total content (19.0%) of the template and the water in $AlAsO_4$-5. The small endothermic effect near 940 °C can be considered as a phase-transition effect of the solid since no corresponding weight loss appears on the t.g.a. curve.

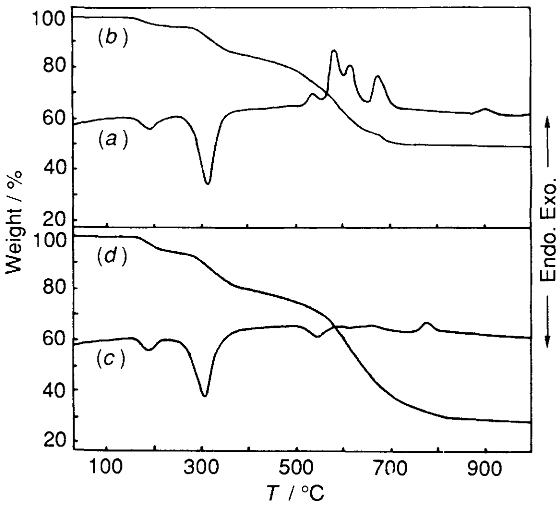

**Figure 5.** D.t.a. [(*a*), (*c*)] and t.g.a. [(*b*), (*d*)] curves for $AlAsO_4$-6 in $N_2$ (bottom) and in air (top)

The compound $AlAsO_4$-5 shows different thermal properties in air from those in $N_2$. At $<430$ °C the d.t.a.–t.g.a. curves are the same as in $N_2$, however the main exothermic effect appears at about 576 °C with a shoulder on the left. Of course, it is the $O_2$ in the air that changes the oxidation-reduction. From the t.g.a. curve one can see that the sublimation of arsenic is much less than that in $N_2$. The total weight loss is about 43%, indicating that a part of the decomposition residue of the template is oxidized by $O_2$ instead of $As^V$.

Figure 5 demonstrates the thermal behaviour of $AlAsO_4$-6 in both $N_2$ and air. The effect at 192 °C caused by the loss of water is accompanied by a weight loss of about 3.8%, also less than the calculated water content (5.4%). Next to this effect is one which can be essentially assigned to the decomposition of the template and the volatilization of the remaining water. However, the corresponding temperature is around 302 °C, 100 °C lower than that of $AlAsO_4$-5, suggesting that the template molecules in $AlAsO_4$-6 may be more loosely attached and as a result more liable to decompose than in $AlAsO_4$-5. The weight loss corresponding to the effect around 302 °C, according to the t.g.a. curve, is 8.9%, much less than the sum

(13.6%) of the calculated template content and the remaining water. This implies that a considerable quantity of the template remains in some form in the framework after the decomposition effect. After calcination at about 310 °C for 2 h, $AlAsO_4$-6 collapses into an amorphous form without decrease in the As/Al ratio, indicating that its framework is more unstable than that of $AlAsO_4$-5. The d.t.a. curve of $AlAsO_4$-6 shows no distinct exothermic effects but the weight loss after the decomposition effect until about 800 °C is remarkable. This means that the oxidation-reduction between the $As^V$ and the remaining template is not drastic but profound due to the large quantity of the latter in the solid. The reaction mechanism remains a matter for further investigation. It is seen from the t.g.a. curve that the total weight loss for $AlAsO_4$-6 in $N_2$ is 72%, 17% more than that for $AlAsO_4$-5. The effects at 540 and 768 °C probably result from phase transitions, since no distinct weight losses occur.

The behaviour of $AlAsO_4$-6 in air is much more complicated than in $N_2$. As for template-occluding zeolites,[26,27] the d.t.a. curve reveals exothermic effects after the endothermic decomposition of the template. Maxima occur at around 528, 572, 604, and 676 °C respectively. Evidently, it is the $O_2$ in the air that leads to these exothermic effects due to its strong oxidizing ability. However, the presence of $O_2$ does not exclude the oxidation-reduction between $As^V$ and the decomposition residue of the template since the total weight loss, though about 19.5% less than that in $N_2$, is still much higher than the sum (17.4%) of the template and the water contents based on the composition, and as a result a considerable amount of arsenic must have sublimed from the solid. Similarly, the weak effect at about 912 °C is attributable to a phase transition for there is no distinct weight loss at around this temperature.

## Conclusion

In the aluminoarsenate gel containing ethylenediamine two framework aluminoarsenates can crystallize hydrothermally by varying the composition of the reaction mixture. They are not isostructural with any of the reported framework alumino- and gallo-phosphates occluding ethylenediamine, as well as other amines or quaternary ammoniums. While the Al and Ga in all ethylenediamine-occluding alumino- and gallo-phosphates are either four- or five-co-ordinated by O atoms, the Al atoms in both $AlAsO_4$-5 and $AlAsO_4$-6 are all six-co-ordinated. The thermal stability of the two new compounds is inferior to that of $AlPO_4$-*n* and $GaPO_4$-*n*. Upon calcination at elevated temperature the framework arsenic sublimes from the solid phases. The presence of $O_2$ can alleviate the sublimation to a certain extent. In summary, because of the difference between $P^V$ and $As^V$, their framework compounds have very different structures and properties even though the template is invariant.

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