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Octahedral As in M^+ arsenates – architecture and seven new members

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Arsenates with arsenic in octahedral coordination are very rare. The present paper provides an overview of all known M^+ arsenates(V) containing octahedrally coordinated arsenic (M^+ = Li, Na, K, Rb, Cs, Ag) and the crystal structures (determined from single-crystal X-ray diffraction data) of the following seven new hydrothermally synthesized members belonging to six different structure types, four of which are novel: $LiH_2As_3O_9$, $LiH_3As_2O_7$, $NaHAs_2O_6$-type $KHAs_2O_6$, $KH_3As_4O_{12}$ and isotypic $RbH_3As_4O_{12}$, $CsAs_3O_8$ and $NaH_2As_3O_9$-type $AgH_2As_3O_9$. The main building unit of these compounds is usually an As_4O_{14} cluster of two edge-sharing AsO_6 octahedra sharing two apical corners each with two AsO_4 tetrahedra. The different connectivity between these clusters defines the different structure types. The novel $CsAs_3O_8$ structure, based on a derivative of the As_4O_{14} cluster, is the most condensed of all these M^+ arsenates, with an O/As ratio of only 2.67 compared with values of 2.75–3.5 for the remaining members. This is achieved through polymerization of the cluster derivatives to infinite chains of edge-sharing AsO_6 octahedra. The $^{[4]}As/^{[6]}As$ ratio drops to only 0.5. All but two of the protonated title compounds show protonated AsO_6 octahedra. Hydrogen bonds range from very strong to weak. An analysis of bond-length distribution and average bond lengths in AsO_6 octahedra in inorganic compounds leads to an overall mean As—O distance for all known AsO_6 octahedra (with R factors < 0.072) of 1.830 (2) Å.

1. Introduction

Extensive studies of the system M^+—M^{3+}—As—O—H (M^+ = Li, Na, K, Rb, Cs, Ag, Tl, NH_4; M^{3+} = Al, Ga, In, Sc, Cr, Fe) have yielded a large number of new M^+–M^{3+} arsenates(V) (Kolitsch, 2004; Kolitsch & Schwendtner, 2004, 2005; Schwendtner & Kolitsch, 2004*a*,*b*, 2005*a*,*b*,*c*, 2007*a*,*b*; Baran *et al.*, 2006*a*,*b*; Schwendtner, 2006; Schwendtner *et al.*, 2006*a*,*b*,*c*), which were characterized structurally but also by spectroscopic and thermoanalytical techniques. As by-products in some of these studies six novel M^+ arsenates(V) were obtained that all contain arsenic in both octahedral and tetrahedral coordination. It is our aim to structurally characterize these materials and have a closer look at AsO_6 units in M^+ arsenates in general. A large number of M^+ arsenates(V) is known, demonstrated by 53 entries in the Inorganic Crystal Structure Database (ICSD, Version 2006-1), most of them featuring arsenic in tetrahedral coordination. All of the 15 (NH_4) arsenates in the database contain only tetrahedrally coordinated arsenic, as do ten out of 13 Na arsenates; these two systems seem to have been studied most extensively. Two of seven Ag arsenates contain AsO_6 octahedra, as does one of

Table 1
Unit-cell parameters of all known M^+ arsenates containing As in octahedral coordination.

Formula	Space group	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å^3)	Z
$LiAsO_3$[a]	$R\bar{3}$	4.808 (3)	4.808 (3)	14.21 (2)	90.00	90.00	120.00	284.48	6
$LiH_2As_3O_9$[b]	$P2_1/n$	9.666 (2)	8.553 (2)	9.970 (2)	90.00	117.86 (3)	90.00	728.7 (3)	4
$LiH_3As_2O_7$[b]	$C2/m$	11.456 (2)	9.133 (2)	5.630 (1)	90.00	115.56 (3)	90.00	531.4 (2)	4
$Na_2As_4O_{11}$[c]	$C2/c$	9.049 (3)	8.287 (3)	11.508 (5)	90.00	102.74 (4)	90.00	842 (2)	4
$Na_7As_{11}O_{31}$[d]	$P\bar{3}m1$	11.199 (3)	11.199 (3)	5.411 (2)	90.00	90.00	120.00	587.80 (3)	1
$NaHAs_2O_6$[e]	$P2_1/c$	5.829 (1)	9.154 (1)	8.989 (1)	90.00	93.29 (1)	90.00	478.85	4
$NaH_2As_3O_9$[f]	$P\bar{1}$	7.167 (1)	7.575 (1)	7.850 (1)	109.89 (1)	107.27 (1)	106.15 (1)	346.9	2
$Na_3H_5As_4O_{14}$[g]	$Pnna$	10.038 (1)	11.692 (2)	9.533 (1)	90.00	90.00	90.00	1118.83	4
$KHAs_2O_6$[b]	$P2_1/c$	6.051 (1)	9.727 (2)	9.054 (2)	90.00	94.21 (3)	90.00	531.46 (18)	4
$KH_3As_4O_{12}$[b]	$P\bar{1}$	5.154 (1)	6.967 (1)	7.532 (2)	63.90 (3)	78.61 (3)	84.35 (3)	238.08 (11)	1
$RbH_3As_4O_{12}$[b]	$P\bar{1}$	5.169 (1)	7.036 (1)	7.766 (2)	63.31 (3)	79.87 (3)	84.38 (3)	248.36 (11)	1
$CsAs_3O_8$[b]	$C2/c$	8.515 (2)	11.690 (2)	7.595 (2)	90.00	112.70 (3)	90.00	697.5 (3)	4
$AgAsO_3$[h]	$Pca2_1$	19.488 (3)	6.600 (1)	12.661 (3)	90.00	90.00	90.00	1628.47	24
$AgH_2As_3O_9$[b]	$P\bar{1}$	7.162 (1)	7.678 (2)	7.880 (2)	110.72 (3)	106.47 (3)	105.43 (3)	354.8 (2)	2
$Ag_4H_4As_4O_{14}$[i]	$P2_1/n$	7.839 (5)	12.428 (5)	6.556 (2)	90.00	109.30 (2)	90.00	602.81	2

References: (*a*) Driss & Jouini (1989*a*); (*b*) this work; (*c*) Driss, Jouini & Omezzine (1988); (*d*) Guesmi *et al.* (2006); (*e*) Nguyen Huy & Jouini (1978); (*f*) Driss, Jouini, Durif & Averbuch-Pouchot (1988); (*g*) Driss & Jouini (1989*b*); (*h*) Curda *et al.*, 2004); (*i*) Boudjada & Averbuch-Pouchot (1984).

the six Li compounds, but none of all six K arsenates. None of the three Tl compounds, the two Cs compounds and the single Rb arsenate contain AsO_6 octahedra. It is interesting to note that octahedrally coordinated arsenic is never encountered together with H_2O in any of these structures. Altogether, there are only seven out of 53 entries featuring the rather rare octahedral coordination of arsenic. An overall analysis of all AsO_4 and AsO_6 polyhedra in structures included in the ICSD leads to the conclusion that only *ca* 3% of all As^V-containing structures feature the AsO_6 polyhedra (Schwendtner, 2007). To our knowledge an analysis and discussion of bond-length distribution and average bond lengths of AsO_6 groups has never been conducted – probably due to the meagre amount of data. Therefore, a bond-length analysis of all AsO_6 bond lengths available in the ICSD was conducted.

The present paper describes the crystal structures of seven new Li, K, Rb, Cs and Ag arsenates containing arsenic in octahedral coordination, and provides an overview on the topology and connectivity of all M^+ arsenates containing AsO_6 octahedra (Table 1).

2. Experimental

2.1. Syntheses

Six of the seven new compounds were initially synthesized by chance as by-products during the syntheses of M^+–M^{3+} arsenates. Five of these seven compounds were later also obtained in relatively large percentages from M^+–As mixtures (see below). All syntheses were undertaken under hydrothermal conditions in Teflon-lined stainless steel autoclaves at 493 K under autogeneous pressure. The Teflon vessels were filled to *ca* 30–50% of their inner volume and were then heated to 493 K, kept at this temperature for 7 d, and slowly cooled to room temperature overnight. Powders of $M^+_2CO_3$ (purities > 99, 99.5, 99.7, 99.9% for M^+ = Li, K, Ag, and Rb, Cs, respectively), crystalline arsenic acid ($H_3AsO_4{\cdot}0.5H_2O$, purity > 99.9%) and (initially) $M^{3+}_2O_3/Cr^{III}(NO_3)_3{\cdot}9H_2O$ were used as starting reagents. We point out that all of the crystals were grown without any added water. Four of the seven compounds could be grown from synthesis batches containing either $M^+_2CO_3$, $M^{3+}_2O_3$ and arsenic acid or $M^+_2CO_3$ and arsenic acid only. Two compounds formed only as by-products during the synthesis of M^+–M^{3+} arsenates, while one compound was only obtained by direct synthesis from $M^+_2CO_3$ and arsenic acid.

Colourless to white rhombic crystals of $LiH_2As_3O_9$ appeared repeatedly in different dry synthesis batches of Li_2CO_3, In_2O_3 and $H_3AsO_4{\cdot}0.5H_2O$ (volume ratio *ca* 2:1:6). The yield of the hygroscopic crystals was *ca* 90%. The same crystals were also obtained from similar mixtures with different M^{3+}cations (Cr, Fe, Sc). Small crystals of $LiH_2As_3O_9$ (yield *ca* 40%, accompanied by 60% of amorphous unidentified material) were also grown from a mixture of Li_2CO_3 and arsenic acid (volume ratio *ca* 1:3) and from the same starting reagents (volume ratio *ca* 1:2), this time accompanied by crystals of $LiAsO_3$ (Driss & Jouini, 1989*a*).

Block, whitish crystals of $LiH_3As_2O_7$ were found in a dry mixture of Li_2CO_3, In_2O_3 and arsenic acid (volume ratio *ca* 4:1:5); yield about 50%. The crystals were accompanied by colourless hexagonal platelets of $LiAsO_3$ (Driss & Jouini, 1989*a*) and colourless mica-like twinned rosettes of a compound with an up-to-now unsolved structure. $LiH_3As_2O_7$ was also obtained from a mixture of Li_2CO_3, Fe_2O_3 and arsenic acid; in this case the crystals were accompanied by those of $LiH_2As_3O_9$. Efforts to synthesize these crystals from synthesis batches free of M^{3+} cations have failed so far. Such attempts have led to the formation of $LiH_2As_3O_9$ accompanied by $LiAsO_3$ (Driss & Jouini, 1989*a*).

$KHAs_2O_6$ formed colourless, translucent, thin tabular crystals from a dry mixture of K_2CO_3, Al_2O_3 and arsenic acid (volume ratio *ca* 2:1:4). Syntheses using $Cr^{III}(NO_3)_3{\cdot}9H_2O$ rather than Al_2O_3 lead to the same result. The same material could also be grown nearly phase-pure (yield *ca* 98%) from a mixture of K_2CO_3 and arsenic acid (volume ratio *ca* 1:4).

$KH_3As_4O_{12}$ was obtained from synthesis batches containing K_2CO_3, Ga_2O_3 and H_3AsO_4 (volume ratio *ca* 2:1:8), and in the equivalent Fe_2O_3-bearing mixture. Similarly, the isotypic

Table 2
Crystal data, data collection information and refinement details for the title compounds.

	$KH_3As_4O_{12}$	$KHAs_2O_6$	$RbH_3As_4O_{12}$	$LiH_2As_3O_9$
Crystal data				
Chemical formula	$KH_3As_4O_{12}$	$KHAs_2O_6$	$RbH_3As_4O_{12}$	$LiH_2As_3O_9$
M_r	533.80	285.95	580.17	377.72
Cell setting, space group	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/c$	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/n$
Temperature (K)	293 (2)	293 (2)	293 (2)	293 (2)
a, b, c (Å)	5.154 (1), 6.967 (1), 7.532 (2)	6.051 (1), 9.727 (2), 9.054 (2)	5.169 (1), 7.036 (1), 7.766 (2)	9.666 (2), 8.553 (2), 9.970 (2)
α, β, γ (°)	63.90 (3), 78.61 (3), 84.35 (3)	90.0, 94.21 (3), 90.0	63.31 (3), 79.87 (3), 84.38 (3)	90.0, 117.86 (3), 90.0
V (Å^3)	238.08 (11)	531.46 (18)	248.36 (11)	728.7 (3)
Z	1	4	1	4
D_x (Mg m^{-3})	3.724	3.574	3.879	3.443
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	14.42	13.31	18.27	13.70
Crystal form, colour	Tabular, colourless	Tabular–rhombic, colourless	Tabular, colourless	Large plate, colourless
Crystal size (mm)	0.04 × 0.03 × 0.02	0.12 × 0.10 × 0.08	0.17 × 0.13 × 0.05	0.15 × 0.08 × 0.08
Data collection				
Diffractometer	NoniusKappaCCD	NoniusKappaCCD	NoniusKappaCCD	NoniusKappaCCD
Data collection method	φ and ω scans	φ and ω scans	φ and ω scans	φ and ω scans
Absorption correction	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)
T_{min}	0.596	0.298	0.147	0.233
T_{max}	0.761	0.416	0.462	0.407
No. of measured, independent and observed reflections	2699, 1385, 1188	3747, 1922, 1785	4335, 2190, 1995	5128, 2642, 2426
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.018	0.011	0.026	0.012
θ_{max} (°)	30.0	32.6	35.0	32.5
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.024, 0.056, 1.12	0.017, 0.043, 1.12	0.028, 0.077, 1.04	0.017, 0.041, 1.13
No. of reflections	1385	1922	2190	2642
No. of parameters	88	87	88	127
H-atom treatment	Mixture of independent and constrained refinement	Refined independently	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0232P)^2 + 0.3298P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0205P)^2 + 0.3321P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0495P)^2 + 0.1743P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0175P)^2 + 0.613P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.0001	0.001	<0.0001	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.16, −0.69	0.71, −0.77	1.37, −1.59	0.67, −0.86
Extinction method	*SHELXL*97	*SHELXL*97	*SHELXL*97	*SHELXL*97
Extinction coefficient	0.0088 (14)	0.0092 (5)	0.059 (3)	0.0087 (3)

	$LiH_3As_2O_7$	$CsAs_3O_8$	$AgH_2As_3O_9$
Crystal data			
Chemical formula	$LiH_3As_2O_7$	$CsAs_3O_8$	$AgH_2As_3O_9$
M_r	271.80	485.67	478.65
Cell setting, space group	Monoclinic, $C2/m$	Monoclinic, $C2/c$	Triclinic, $P\overline{1}$
Temperature (K)	293 (2)	293 (2)	293 (2)
a, b, c (Å)	11.456 (2), 9.133 (2), 5.630 (1)	8.515 (2), 11.690 (2), 7.595 (2)	7.162 (1), 7.678 (2), 7.880 (2)
α, β, γ (°)	90.0, 115.56 (3), 90.0	90.0, 112.70 (3), 90.0	110.72 (3), 106.47 (3), 105.43 (3)
V (Å^3)	531.4 (2)	697.5 (3)	354.8 (2)
Z	4	4	2
D_x (Mg m^{-3})	3.398	4.625	4.481
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	12.55	19.44	16.75
Crystal form, colour	Irregular fragment, colourless	Large strongly distorted octahedron, colourless–white	Dogtoothed-shaped, colourless
Crystal size (mm)	0.08 × 0.07 × 0.06	0.10 × 0.08 × 0.07	0.15 × 0.13 × 0.08
Data collection			
Diffractometer	NoniusKappaCCD	NoniusKappaCCD	NoniusKappaCCD
Data collection method	φ and ω scans	φ and ω scans	φ and ω scans
Absorption correction	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)

Table 2 (continued)

	$LiH_3As_2O_7$	$CsAs_3O_8$	$AgH_2As_3O_9$
T_{min}	0.433	0.247	0.188
T_{max}	0.520	0.343	0.348
No. of measured, independent and observed reflections	1933, 1020, 924	3021, 1540, 1433	4992, 2568, 2375
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.011	0.013	0.021
θ_{max} (°)	32.6	34.9	32.5
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.017, 0.041, 1.14	0.020, 0.054, 1.03	0.029, 0.073, 1.09
No. of reflections	102	1540	2568
No. of parameters	61	57	127
H-atom treatment	Refined independently	No H atoms present	Mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.017P)^2 + 0.9444P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0294P)^2 + 3.3231P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0459P)^2 + 0.211P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	<0.0001	<0.0001	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.04, −0.54	2.18, −2.13	1.58, −2.35
Extinction method	*SHELXL*97	*SHELXL*97	*SHELXL*97
Extinction coefficient	0.0034 (3)	0.0076 (3)	0.068 (2)

Computer programs used: *COLLECT* (Nonius, 2002), *HKL DENZO* and *HKL SCALEPACK* (Otwinowski & Minor, 1997), *SHELXS*97 (Sheldrick, 1997*b*), *SHELXL*97 (Sheldrick, 1997*a*), *DIAMOND* (Brandenburg, 2005).

$RbH_3As_4O_{12}$ compound formed from mixtures of K_2CO_3, Sc_2O_3 [or $Cr^{III}(NO_3)_3{\cdot}9H_2O$] and arsenic acid (volume ratio *ca* 2:1:4). $RbH_3As_4O_{12}$ was also grown from a mixture of K_2CO_3 and arsenic acid (volume ratio *ca* 1:4, yield *ca* 80%).

$CsAs_3O_8$ formed large white-to-colourless pseudo-octahedral crystals in a mixture of Cs_2CO_3, Fe_2O_3 and arsenic acid (volume ratio *ca* 1:1:4). The compound was accompanied by large pale bluish pseudo-octahedral crystals of $CsFe_2As(HAsO_4)_6$ (Schwendtner & Kolitsch, 2007*c*), with a crystal structure derived from that of $RbFe(HPO_4)$ (Lii & Wu, 1994). $CsAs_3O_8$ was also grown from a mixture of Cs_2CO_3 and arsenic acid (volume ratio *ca* 1:3, yield *ca* 70%). The material is hygroscopic and transforms in air within weeks into the novel compound $Cs(H_2AsO_4)(H_3AsO_4)_2$ (Schwendtner & Kolitsch, 2007*d*).

Colourless dogtooth-shaped to tabular (101) crystals of $AgH_2As_3O_9$ were grown from a mixture of Ag_2CO_3 and arsenic acid (volume ratio *ca* 1:3, yield *ca* 95%).

2.2. X-ray diffraction experiments and crystal structure solution

Several crystals of each of the seven compounds were selected for single-crystal studies with a Nonius KappaCCD single-crystal four-circle diffractometer [Mo tube, graphite monochromator, CCD detector frame size: 621 × 576 pixels (binned mode)], equipped with a 300 µm diameter capillary-optics collimator to provide increased resolution. A complete sphere of reciprocal space (φ and ω scans) was measured at room temperature for a suitable crystal of each compound (see Table 2 for details). The intensity data were processed with the Nonius program suite *DENZO-SMN* (Otwinowski & Minor, 1997) and corrected for Lorentz, polarization and background effects, and, by the multi-scan method (Otwinowski & Minor, 1997; Otwinowski *et al.*, 2003), for absorption. The crystal structures were solved with *SHELXS*97 (Sheldrick, 1997*b*) and subsequent Fourier and difference Fourier syntheses, followed by anisotropic full-matrix least-squares refinements on F^2 using *SHELXL*97 (Sheldrick, 1997*a*; Table 1). All H atoms could be detected and were successfully refined, in the cases of $KH_3As_4O_{12}$, $RbH_3As_4O_{12}$ and $LiH_2As_3O_9$ with restraints on the O—H bond distances [O—H = 0.90 (2) Å using the *SHELXL*97 *DFIX* command].

The crystals were of generally good quality and showed no signs of twinning. The last step of refinement resulted in final residuals $R1(F)$ of < 0.029 for all seven compounds (Table 2). All the largest residual peaks (electron densities 2.18/−2.13 e Å^{-3}) in the final difference-Fourier map found for $CsAs_3O_8$ were close to the Cs positions, whereas the largest peaks for $RbH_3As_4O_{12}$ were close to O1 and As1. $KHAs_2O_6$ and $LiH_2As_3O_9$ did not show any distinct electron densities > |1| e Å^{-3}; those of $KH_3As_4O_{12}$ and $LiH_3As_2O_7$ were only slightly larger (Table 2). Mean bond lengths and angles, calculated bond valences based on published parameters (Brown & Aldermatt, 1985) and distortion parameters of bond lengths (Brown & Shannon, 1973) and bond angles (Robinson *et al.*, 1971) for all As-centred polyhedra are presented in Table 3; hydrogen bonds are given in Table 4 and a detailed table of bond lengths and bond angles has been deposited as supplementary material.[1]

3. Results and discussion

3.1. Crystal structure descriptions

All of the protonated new structure types are built up by the well known As_4O_{14} cluster (Fig. 1), which was first described

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: SN5044). Services for accessing these data are described at the back of the journal.

for $BaH_6As_4O_{14}$ (Blum *et al.*, 1977), or a derivative of that cluster, as is the case for $CsAs_3O_8$. The cluster consists of two edge-sharing AsO_6 octahedra, the apices of both octahedra being connected on two sides *via* AsO_4 tetrahedra. In the following structures these clusters are either isolated and only connected by hydrogen bonds and the M^+ cations (as is the case for $LiH_3As_2O_7$) or they form chains as in $KH_3As_4O_{12}$, isotypic $RbH_3As_4O_{12}$ and $AgH_2As_3O_9$. Layer structures are formed by $LiH_2As_3O_9$ and $KHAs_2O_6$, whereas in $CsAs_3O_8$ the clusters are reduced and polymerize to form a microporous framework.

3.1.1. Structure of $LiH_2As_3O_9$. In $LiH_2As_3O_9$ each As_4O_{14} cluster is corner-connected to four other clusters, thus forming a (101) layer (Fig. 2*a*). Additionally, the remaining unconnected two corners of the AsO_6 octahedra are shared with doubly protonated AsO_4 groups, which, as shown in Fig. 2(*b*), connect these layers *via* medium–strong to weak hydrogen bonds (Table 4). These H_2AsO_4 groups are also the main difference between this structure type and the related $KHAs_2O_6$ structure (see below), where the H_2AsO_4 groups are replaced by H atoms. $LiH_2As_3O_9$ and stoichiometrically identical $AgH_2As_3O_9$ (see §3.1.6) are the only ones of the title compounds that contain hydrogen but no protonated AsO_6 octahedra. The As—O distances are rather long for both tetrahedrally coordinated As atoms ($\langle$As1—O$\rangle$ = 1.694, $\langle$As2—O$\rangle$ = 1.689 Å) compared with the average distance for inorganic compounds of 1.682 Å (Baur, 1981). The longest As—O distances in both AsO_4 groups involve the O atoms corner-shared with the AsO_6 octahedra. This is explained by As^V–As^V repulsion within the As_4O_{14} cluster, similar to the situation in diarsenates (long As—O_{bridge} distances). Still above average, but slightly shorter, are the As—OH distances, while the shortest distances are to the O atoms shared with the Li-centred polyhedra. The Li^+ cations are in [4 + 1] coordination [Li—O 1.958 (4)–2.072 (4) Å; the fifth distance is much larger at 2.643 (4) Å] and form edge-sharing dimers (Li_2O_6), not uncommon for inorganic Li compounds (Wenger & Armbruster, 1991). These dimers form – together with the H_2AsO_4 groups – a second layer sandwiched between two (101) octahedral–tetrahedral layers, and also connect the latter to a stable framework structure. The bond-valence sum (BVS) for Li is close to ideal with 0.97 v.u. (0.93 v.u without the fifth O). The BVSs of the protonated O atoms are 1.19/1.36 as expected (Table 3, bottom), whereas the relatively low BVS of O1 (1.69 v.u.) can be explained by its role as acceptor of the strongest hydrogen bond (Table 4). The somewhat overbonded O2 (2.12 v.u.) shares relatively short bonds with two As atoms.

3.1.2. Structure of $LiH_3As_2O_7$. In this novel structure type the As_4O_{14} clusters are isolated, which is reflected by the high O/As ratio of 3.5. The Li^+ cations are four-coordinated [Li—O 1.985 (2)–1.993 (4) Å; BVS 0.97 v.u.] and form Li_2O_6 dimeric units as in $LiH_2As_3O_9$. These dimers corner-connect adjacent clusters along the *b* and *c* axes, thus forming (100) layer-like units (Fig. 3*a*). Adjacent layer-like units are offset by *b*/2, so that the $HAsO_4$ tetrahedra of the clusters can form bonds to the edge-sharing corners of the Li_2O_6 dimeric units, thereby forming a stable framework (Fig. 3*a*). Additionally, two different hydrogen bonds reinforce the framework (Figs. 3*a* and *b*); the AsO_6 octahedron is diprotonated and forms medium–strong hydrogen bonds, whereas the $HAsO_4$ tetrahedron forms strong hydrogen bonds (Table 4). Interestingly, the shortest As–O distances of the H_2AsO_6 group are those to the protonated O with only 1.768 (1) Å, and also the average As—O distance of this polyhedron is rather short with 1.820 Å (mean $^{[6]}$As—O distance is 1.830 Å, see discussion in §3.3 for details). The H_2AsO_6 polyhedron shows a slightly stronger distortion than that in $LiH_2As_3O_9$. The most underbonded O atoms are the donors of the hydrogen bonds; the low BVS of O5 (1.68 v.u.) can be explained by its role as an acceptor of a very strong hydrogen bond.

3.1.3. Structure of $KHAs_2O_6$. This compound is isotypic to $NaHAs_2O_6$ (Nguyen Huy & Jouini, 1978) and is built up by As_4O_{14} clusters, which are corner-connected *via* their AsO_4 groups to interrupted (100) sheets, as in $LiH_2As_3O_9$ (*cf.* Figs. 2*a* and 4*a*). However, the connectivity between these zigzag sheets is different (*cf.* Figs. 2*b* and 4*b*); in $KHAs_2O_6$ the empty corners of both the AsO_6 octahedra of the cluster form hydrogen bonds which connect adjacent sheets, the seven-coordinated K^+ cations being located between two sheets, whereas in $LiH_2As_3O_9$ additional AsO_4 tetrahedra are sharing these corners and only these form the hydrogen bonds. The single hydrogen bond in $KHAs_2O_6$ is rather strong and is confirmed by the low BVS of the donor atom (O5, 1.22 v.u.). Again, the As—O distance to the protonated O atoms is the shortest one in the AsO_6 octahedron. The As—O distances in the AsO_4 group comprise one very short distance (involving the slightly underbonded O1 atom with 1.77 v.u., which is an acceptor of the hydrogen bond) and three nearly equally long bonds to the O atoms shared with the AsO_6 octahedra. In the first description of this structure type (Nguyen Huy & Jouini, 1978) the H atoms in $NaHAs_2O_6$ were not found, nor was the possible position of the H atom discussed. The mean bond length for the AsO_4 tetrahedra is slightly larger in $NaHAs_2O_6$

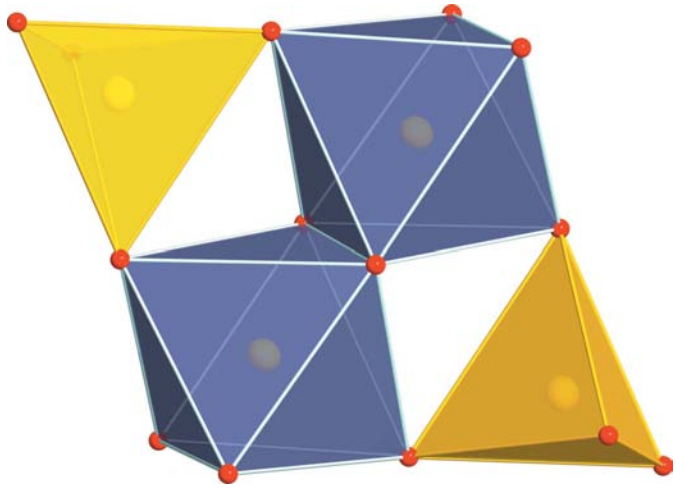

Figure 1
The As_4O_{14} cluster, which is the predominant building unit in AsO_6-containing M^+ arsenates.

Table 3
Mean distances (Å) and angles (°), bond-valence sums and distortion parameters of the seven new title compounds.

Bond-length distortion (Brown & Shannon, 1973) for tetrahedra: $\Delta = \frac{1}{4}\sum_{i=1}^{4}\left[(R_i - \overline{R})/\overline{R}\right]^2$; for octahedra: $\Delta = \frac{1}{6}\sum_{i=1}^{6}\left[(R_i - \overline{R})/\overline{R}\right]^2$. Bond-angle distortion (Robinson *et al.*, 1971) for tetrahedra: $\sigma^2 = \sum_{i=1}^{6}(\theta_i - 109.47^\circ)^2/5$; for octahedra: $\sigma^2 = \sum_{i=1}^{12}(\theta_i - 90^\circ)^2/11$.

	$LiH_2As_3O_9$	$LiH_3As_2O_7$	$KHAs_2O_6$	$KH_3As_4O_{12}$	$RbH_3As_4O_{12}$	$CsAs_3O_8$	$AgH_2As_3O_9$
As1							
$\langle^{[4]}$As1—O$\rangle$ (Å)	1.694	1.694	1.690	1.690	1.692	1.687	1.692
BVS As1 (v.u.)	4.90	4.90	4.94	4.93	4.91	4.96	4.93
Distortion (Δ)	4.48E-04	4.45E-04	2.97E-04	1.36E-04	1.18E-04	6.05E-06	5.92 E-06
As2/3†							
$\langle^{[4]}$As2/3-O$\rangle$ (Å)	1.689						1.696
BVS (v.u.)	4.95						4.87
Distortion (Δ)	3.73E-04						4.29E-04
As2/3†							
$\langle^{[6]}$As2/3—O$\rangle$ (Å)	1.822	1.821	1.828	1.831	1.830	1.835	1.824
BVS (v.u.)	5.19	5.22	5.12	5.09	5.10	5.03	5.15
Distortion (Δ)	1.38E-04	4.74E-04	4.84E-04	7.84E-04	7.42E-04	6.19E-04	1.01E-04
As1							
$\langle$O—$^{[4]}$As1—O$\rangle$ (°)	109.22	109.27	109.35	109.44	109.44	109.41	109.38
Distortion (σ^2)	43.85	24.13	31.91	5.91	5.89	15.39	38.42
As2/3†							
$\langle$O—$^{[4]}$As2/3—O$\rangle$ (°)	109.18						109.30
Distortion (σ^2)	47.58						35.09
As2/3†							
$\langle$O—$^{[6]}$As2/3—O$\rangle$ (°)	90.02	90.04	90.03	89.98	90.02	90.12	90.02
Distortion (σ^2)	7.87	21.38	40.21	8.55	9.11	24.64	35.09
Bond-valence sums for O atoms (v.u.)							
	O1 1.69	O1 1.92	O1 1.77	O1 2.07	O_H1 1.48	O_H1 1.44	O1 1.89
	O2 2.12	O2 1.93	O2 2.12	O2 2.01	O2 2.14	O2 2.09	O_H2 1.29
	O3 1.96	O_H3 1.14	O3 1.93	O3 1.87	O3 1.87	O3 1.87	O3 1.69
	O4 1.91	O_H4 1.24	O4 2.03	O4 2.15	O4 2.03	O4 2.04	O4 2.05
	O5 1.92	O5 1.68	O_H5 1.20	O_H5 1.22	O_H5 1.27		O5 1.86
	O_H6 1.19		O6 1.81	O6 1.96	O6 1.83		O6 2.01
	O_H7 1.36						O_H7 1.27
	O8 2.09						O8 1.95
	O9 1.78						O9 1.93

† The second AsO_4 polyhedron in $LiH_2As_3O_9$ is numbered As2, whereas it is numbered As3 in $AgH_2As_3O_9$; the AsO_6 polyhedra are numbered As2 in all compounds except $LiH_2As_3O_9$, where it is called As3.

than in $KHAs_2O_6$ (1.70 *versus* 1.690 Å), whereas the opposite is true for the AsO_6 octahedra (1.82 *versus* 1.831 Å). $KHAs_2O_6$ clearly is a sheet structure, whereas the related $LiH_2As_3O_9$ structure can also be regarded as a framework if the LiO_4 tetrahedra are considered as part of the framework.

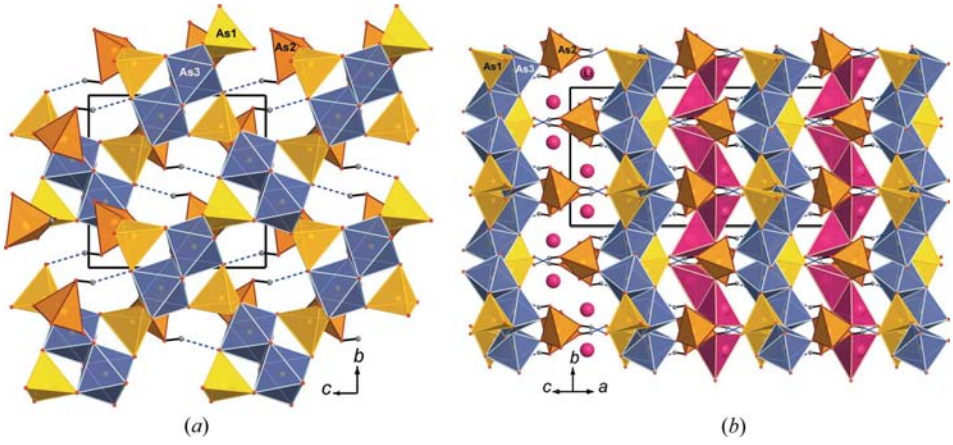

Figure 2
$LiH_2As_3O_9$: (*a*) view along [100], documenting the connectivity within the (100) octahedral–tetrahedral layer; (*b*) view along [101], showing the sequence of octahedral–tetrahedral layers and layers containing H_2AsO_4 and Li_2O_6 dimers (Li^+ cations shown in left part of figure).

3.1.4. Structures of $KH_3As_4O_{12}$ and $RbH_3As_4O_{12}$. In these two new compounds, representing a novel structure type, the sheet structure of $KHAs_2O_6$ is broken up into chains. The As_4O_{14} clusters are corner-linked *via* the AsO_4 tetrahedra to form infinite chains parallel to the *a* axis. All the empty corners of both AsO_6 octahedra and AsO_4 tetrahedra are protonated and involved in hydrogen bonds. The resulting network provides reinforcement along the *b* and *c* axes (Fig. 5*a*). Unlike $KHAs_2O_6$, where the hydrogen donor belongs to the AsO_6 octahedron and the acceptor to AsO_4, here a medium–strong hydrogen bond exists between two AsO_6 groups and a very strong, symmetry-restricted hydrogen bond involving a characteristically split half-occupied H position between two AsO_4 groups [O1—H2···O1 2.453 (4)/2.458 (5) Å for the Rb and K compounds, respectively]. The shortest As—O bonds

Table 4
Hydrogen bonds of the six new protonated M^+ arsenates.

Compound	D—H	$d(D$—H) (Å)	d(H···A) (Å)	∠DHA (°)	$d(D$···A) (Å)	A
$LiH_2As_3O_9$	O6—H1	0.877 (19)	2.11 (3)	157 (4)	2.936 (2)	O4
	O7—H2†	0.86 (4)	1.85 (4)	161 (3)	2.676 (2)	O1
$LiH_3As_2O_7$	O4—H1†	0.74 (3)	2.11 (3)	174 (3)	2.8410 (19)	O3
	O3—H2†	0.68 (5)	1.87 (5)	171 (5)	2.552 (2)	O5
$KHAs_2O_6$	O5—H1†	0.77 (3)	1.91 (3)	167 (3)	2.6669 (18)	O1
$KH_3As_4O_{12}$	O5—H1	0.885 (14)	1.949 (19)	164 (4)	2.810 (3)	O3
	O1—H2	0.89 (2)	1.58 (2)	166 (7)	2.458 (5)	O1
$RbH_3As_4O_{12}$	O5—H1	0.852 (19)	1.98 (2)	169 (4)	2.822 (3)	O3
	O1—H2	0.901 (10)	1.58 (3)	161 (8)	2.453 (4)	O1
$AgH_2As_3O_9$	O2—H1†	0.879 (19)	1.70 (2)	162 (5)	2.551 (4)	O3
	O7—H2	0.87 (6)	1.97 (7)	157 (6)	2.796 (3)	O6

† Not restrained

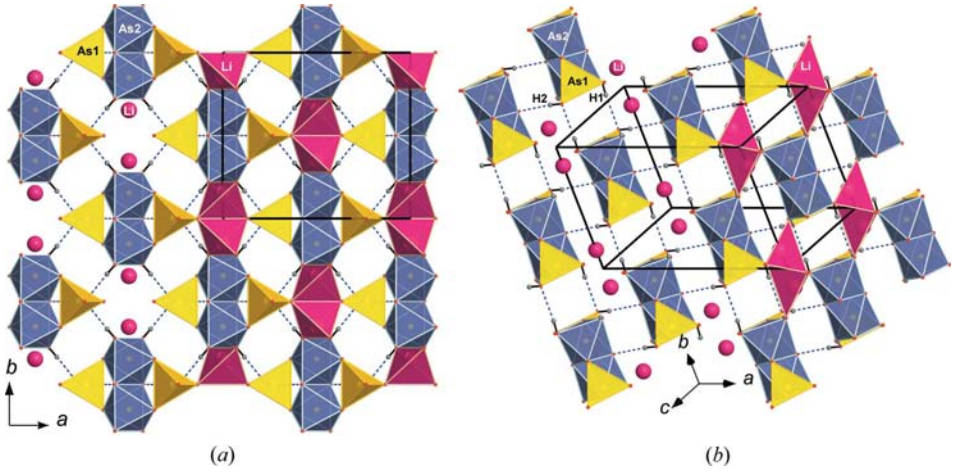

Figure 3
$LiH_3As_2O_7$: (*a*) view along **c**, showing isolated As_4O_{14} clusters; (*b*) view along [112] showing hydrogen-bonding scheme. The Li^+ cations are partly shown as polyhedra in both pictures.

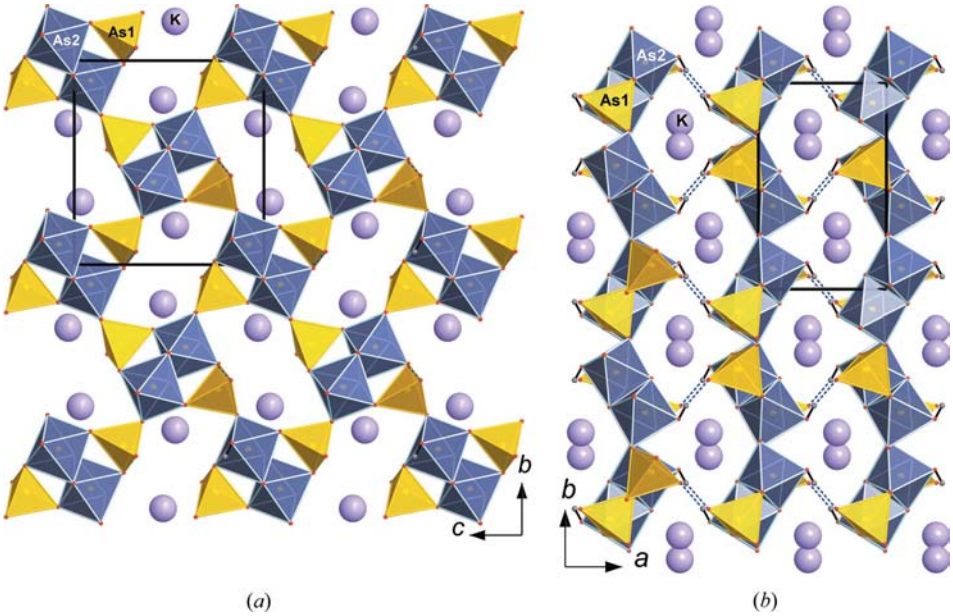

Figure 4
$KHAs_2O_6$: (*a*) view along **a** and connectivity of As_4O_{14} clusters to (100) sheets (*cf.* Fig. 2*a*); (*b*) view along **c** and connection between sheets, with K atoms in voids (*cf.* Fig. 2*b*).

of the AsO_4 and AsO_6 polyhedra of both compounds involve the protonated O atom, whereas the longest bonds are to the bridging O atoms of the other arsenate groups. The K/Rb atoms are located in (100) planes, separating the chains. They have a rather large, irregular coordination sphere comprising ten oxygen ligands. The average Rb—O distance of 3.07 Å is close to the expected value of *ca* 3.03 Å (Khan & Baur, 1972) and only slightly longer than the corresponding distance of the K^+ cation (⟨K—O⟩ = 2.99 Å). Owing to these slight differences in the mean bond lengths the BVS is rather large for the Rb atom (1.21 v.u.), but as expected for the K atom (1.01 v.u.).

3.1.5. Structure of $CsAs_3O_8$. The structure of $CsAs_3O_8$ is the most unusual among the title compounds because it is a rather condensed framework structure. It can most easily be described as being built up by As_3O_{12} rings (visualized as an As_4O_{14} cluster with one AsO_4 tetrahedron missing). These rings share edges with AsO_6 octahedra of two adjacent rings to form infinite zigzag AsO_6 chains running parallel to [100] (Fig. 6*a*). The chains are firmly connected to each other by AsO_4 tetrahedra (Figs. 6*b* and *c*), thus forming a rather dense framework structure with the lowest O/As ratio (2.67) of all known M^+ arsenates(V) containing arsenic in octahedral coordination. Nevertheless, it represents a microporous structure type with ten-coordinated Cs cations located at the intersections of channels parallel to [110] and [001] (⟨Cs—O⟩ = 3.300 Å). As every AsO_4 tetrahedron shares its corners with four AsO_6 octahedra and each AsO_6 octahedron shares edges with two other symmetry-equivalent AsO_6 octahedra and corners with two different AsO_4 tetrahedra, there is no room for hydrogen bonds. As expected for four identical ligand atoms, the As—O bond lengths of AsO_4 are very similar and the bond-length distortion is also rather low, unlike all six other compounds where there is at least one very short and a few very long As—O bonds (see supplementary

table). The mean $^{[4]}$As—O bond length (1.687 Å) is still above the average 1.682 Å (Baur, 1981), but considerably shorter than in the other compounds. The longest As—O bond lengths in the AsO_6 octahedra are the ones to O atoms shared with the AsO_4 tetrahedra, as can be expected by the stronger influence of the As^V atom in this cation, compared with that in the AsO_6 octahedra. The stoichiometry of this compound is so far unprecedented among the M^+ arsenates discussed herein.

3.1.6. Structure of $AgH_2As_3O_9$. This structure type is isotypic to that of $NaH_2As_3O_9$ (Driss, Jouini, Durif & Averbuch-Pouchot, 1988). Its sum formula is similar to $LiH_2As_3O_9$, but the structure types are not related. Both types are built up by As_4O_{14} units, but where those are connected to layers in $LiH_2As_3O_9$, they are connected by two $As1O_4$ groups to infinite chains parallel to *a* (Figs. 7*a* and *b*) in $AgH_2As_3O_9$. The H atoms very firmly connect these chains in directions **b** and **c** through strong to medium–strong hydrogen bonds (Table 4). The Ag cation is six-coordinated as is the Na^+ cation in the isotypic Na compound and the AgO_6 polyhedron can be best described as a strongly distorted octahedron (Δ = 0.0041, Brown & Shannon, 1973; σ^2 = 228.2, Robinson *et al.*, 1971; mean Ag—O = 2.515 Å compared with 2.435 Å in the Na compound). The As—O bond lengths in AsO_4 tetrahedra are both longer (1.692 and 1.696 Å) than the literature values (Baur, 1981) and are longest for the tetrahedron of the As_4O_{14} cluster. This pattern is similar to the situation in the isotypic Na compound, where the differences between As1 and As3 are even more pronounced. As expected from the larger ionic radius of six-coordinated Ag^+ compared with Na^+ (Shannon, 1976), the cell volume of the new compound $AgH_2As_3O_9$ is larger than that of $NaH_2As_3O_9$ (Table 1). Cell lengths *b* and *c* are elongated in the Ag compound, whereas the *a* cell length is slightly shorter than in the Na compound. This can be explained by the arrangement of the $[H_2As_3O_9]^-$ chains in the structure: These chains run parallel to *a*; this cell parameter is therefore hardly influenced by the size of the M^+ cation.

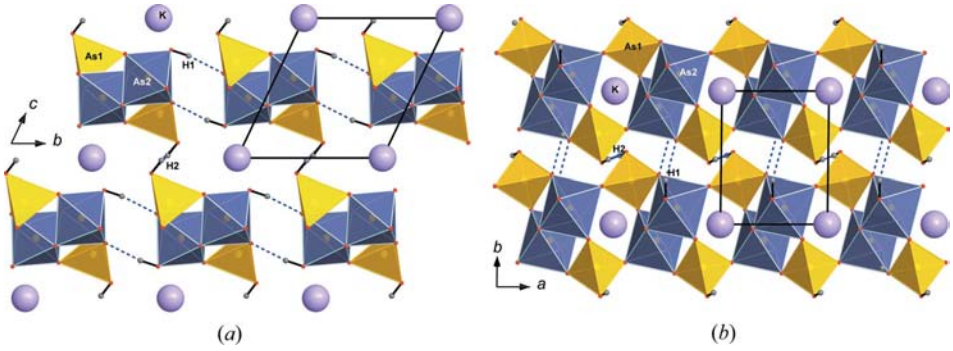

Figure 5
$KH_3As_4O_{12}$: (*a*) view parallel to infinite chains extending parallel to **a**, showing linkage between chains *via* hydrogen bonds (note the split H2 position); (*b*) view along **c**, perpendicular to chains, showing the connectivity of the chains.

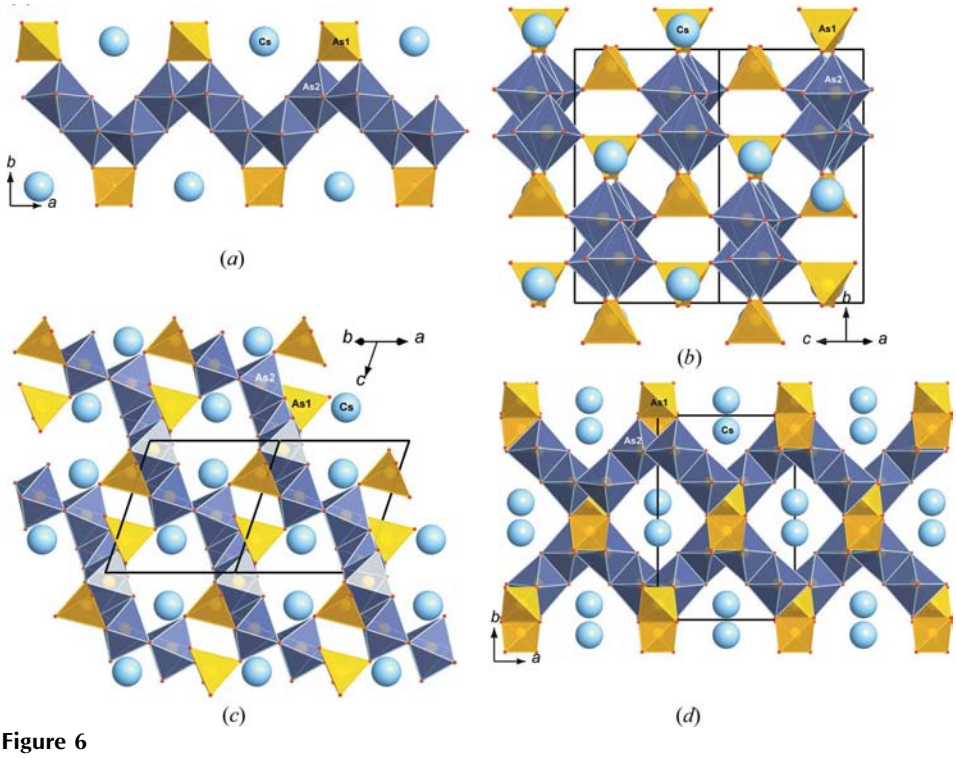

Figure 6
$CsAs_3O_8$: (*a*) view along **c** showing zigzag AsO_6 chains running parallel to **a**; (*b*) view along [101] demonstrating connection between the chains *via* AsO_4 tetrahedra; (*c*) view along [110] with Cs-filled microporous channels; (*d*) view along [001] with Cs-filled microporous channels.

3.2. Comparison and discussion of all 15 structure types containing As in octahedral coordination

Comparing the seven novel compounds to the eight other known compounds containing M^+ cations and arsenic(V) in octahedral coordination (Table 1) demonstrates that six different building units are present; the most prevalent is the As_4O_{14} cluster, which is encountered in 10 of the 15 compounds. In these structure types, every AsO_6 octahedron shares only one edge with another AsO_6 octahedron. The connectivity between the As_4O_{14} units is the main difference in these ten compounds. $Ag_4H_4As_4O_{14}$ (Boudjada & Averbuch-Pouchot, 1984), $Na_3H_5As_4O_{14}$ (Driss & Jouini, 1989*b*) and the novel $LiH_3As_2O_7$ all represent structures with

isolated As_4O_{14} groups. Connectivity between the groups is provided through the M^+ cations and hydrogen bonds. Their structures and stoichiometries are different. For every As_4O_{14} unit the ratio of H:M^+ differs in these three compounds and is largest (3) in the Li compound and smallest (1) in the Ag compound. The influence of the hydrogen bonds reinforcing the structure is therefore more pronounced in the Li compound, whereas the M^+ cations play a more important part in the Ag compound. $Na_3H_5As_4O_{14}$ lies somewhere in-between. The two structure types $M^+H_2As_3O_9$ (M^+ = Na, Ag) and $M^+H_3As_4O_{14}$ (M^+ = K, Rb) are both chain structures; the As_4O_{14} groups are linked to infinite chains *via* the AsO_4 groups of the cluster. The difference arises through the connectivity of the chains, which is directly through hydrogen bonds in the $M^+H_3As_4O_{14}$ structure, whereas additional AsO_4 groups attached to the cluster connect adjacent chains through hydrogen bonds in the $M^+H_2As_3O_9$-type structure (M^+ = Na, Ag). This fact is also the main difference in the two sheet-structure types $M^+HAs_2O_6$ (M^+ = Na, K) and $LiH_2As_3O_9$, where the As_4O_{14} groups link to sheets through the AsO_4 groups of the cluster. However, connectivity between adjacent sheets is only achieved through hydrogen bonds in the $M^+HAs_2O_6$ type and *via* an additional AsO_4 group, that forms hydrogen bonds, in the $LiH_2As_3O_9$-type structure.

The following five structure types do not contain As_4O_{14} groups. The building unit of $CsAs_3O_8$ consists of infinite zigzag chains of edge-sharing AsO_6 octahedra; therefore, every AsO_6 shares two edges with two more AsO_6 octahedra. This is taken a step further in the recently described, oxygen-deficient $Na_7As_{11}O_{31}$ (Guesmi *et al.*, 2006), where some of the octahedra share edges with two neighbouring AsO_6 groups and the others have three common edges with other AsO_6 groups. $Na_7As_{11}O_{31}$ can therefore be considered the missing link between $CsAs_3O_8$ and $LiAsO_3$ (Driss & Jouini, 1989*a*). In the latter the structure is built up by sheets of edge-sharing AsO_6 octahedra, and each AsO_6 group shares edges with three neighbouring AsO_6 groups. This structure type is also the only one based solely on octahedrally coordinated arsenic. With respect to edge connections of the AsO_6 unit the structure of $AgAsO_3$ (Curda *et al.*, 2004) is probably the most unusual, as it represents the only type based on infinite chains of corner- (instead of edge-) sharing AsO_6 octahedra, which are linked by AsO_4 tetrahedra, similar to the As_4O_{14} clusters. The structure type of $Na_2As_4O_{11}$ (Driss, Jouini & Omezzine, 1988) can be seen as the link between the $AgAsO_3$ structure and those structures based solely on edge-sharing AsO_6 polyhedra. It consists of two edge-sharing AsO_6 octahedra which are linked through a common corner to infinite chains. These chains are connected by AsO_4 tetrahedra to a framework structure.

The chemical formula of the M^+ arsenates gives, analogous to silicates, some indication about the polymerization of the As_4O_{14} cluster units. The O/As ratio is highest for the isolated clusters (3.5), medium for chain- and layer-structures (3) and lowest for framework structures (< 3), as expected. The same applies for the H/As ratio, which is highest in structure types with isolated As-based clusters and, with increasing polymerization, decreases down to zero for the framework structures (*e.g.* $CsAs_3O_8$). The oxygen-deficient $Na_7As_{11}O_{31}$ is the only type that does not completely obey this rule.

Unlike other protonated arsenates, where As—OH distances are usually longer than As—O distances (⟨As—OH⟩ = 1.731 Å; Ferraris & Ivaldi, 1984), the exact opposite is encountered in the present structure types. The strong influence of the As^V atom with its strong covalent bonds results in a competition for the shared O atoms. This can be seen very easily in all protonated AsO_4 tetrahedra, where the As—OH distances are usually a lot shorter than average, while the bonds between As atoms and O atoms shared with other As atoms are significantly longer, as expected from As–As repulsion (see supplementary table). It would be expected that this influence is stronger if AsO_4 tetrahedra (instead of AsO_6 octahedra) are involved as ligands and indeed this is very clearly the case as shown in $CsAs_3O_8$. The average As—O bond lengths of all AsO_4 tetrahedra in these arsenates are above the average value of 1.682 Å (Baur, 1981) and range between 1.687 and 1.696 Å. It is interesting to note that a rather large average As—O distance occurs in the Li compounds, whereas the smallest average distance can be observed in the Cs compound. Exactly the opposite is true for the AsO_6 octahedra, where the average As—O distances range between 1.821 ($LiH_3As_2O_7$) and 1.835 Å ($CsAs_3O_8$). This can at least partly be explained by the different ligands. In the case of Cs the only slightly distorted AsO_4 tetrahedron leads to a smaller average bond length, in agreement with the distortion theorem (Brown & Shannon, 1973; Brown, 1981); on the other hand, the linkage of the AsO_6 octahedra with six different As atoms does not considerably

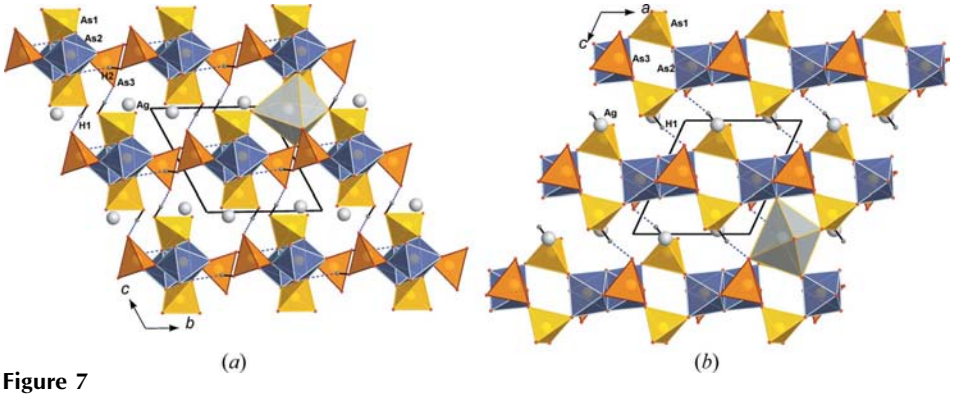

Figure 7
$AgH_2As_3O_9$: (*a*) view along [100], documenting the existence of chains, connected *via* hydrogen bonds and octahedrally coordinated Ag^+ cations, running parallel to **a**; (*b*) view along [010], showing the chains consisting of As_4O_{14} groups connected *via* the $As1O_4$ groups. The chains are connected *via* hydrogen bonds of $As3O_4$ groups. Both figures contain an additional single polyhedral representation of the AgO_6 polyhedron.

change its distortion values, but leads to an increase of the mean bond length through the above described influences of the As^V cation (As–As repulsion). For unknown reasons not a single one of the 15 (NH_4) arsenates in the ICSD database contains arsenic in octahedral coordination and our studies of this system have not yielded any new NH_4–[6]As compounds so far.

3.3. Bond-length distribution in AsO_6 octahedra

An analysis of all As—O bond lengths in AsO_6-containing arsenates available in the ICSD was conducted. Structures fulfilling the following requirements were considered: refined structure, conventional R factor < 0.072, coordination spheres comprise exactly six O atoms, no partial substitution of the As or O atoms. All in all, only 24 AsO_6 polyhedra belonging to 23 different compounds in the ICSD database meet these conditions. Together with the seven new compounds and the recently described $Na_7As_{11}O_{31}$ (Guesmi *et al.*, 2006), 33 AsO_6 octahedra of 31 compounds (four of these have R values > 5) fulfil the requirements and were used for the analysis. It is worth noting that there are more than 900 AsO_4 polyhedra that meet similar requirements – AsO_6 polyhedra therefore occur only in less than 3% of all arsenates (Schwendtner, 2007). Besides the 15 M^+ arsenate compounds listed in Table 1 the following compounds were used: $BaH_6As_4O_{14}$ (Blum *et al.*, 1977); $Mg_{8.5}(AsO_4)_2(AsO_6)O_2$ (Bless & Kostiner, 1973); $Ni_{8.5}(AsO_4)_2(AsO_6)O_2$ (Fleet & Barbier, 1989); $K_7(AsV_{14}O_{40})(H_2O)_{12}$ (Mueller *et al.*, 1991); $Co_5(AsVO_{10})$ (Osterloh & Müller-Buschbaum, 1994); $Ni(AsO_3)_2$, $Co(AsO_3)_2$ and $Mn(AsO_3)_2$ (Nakua & Greedan, 1995); $Pb(As_2O_6)$ and $Ca(As_2O_6)$ (Losilla *et al.*, 1995); $Cd(As_2O_6)$ (Weil, 2001); $Hg(As_2O_6)$ (Mormann & Jeitschko, 2000); $Hg_2(As_2O_6)$ and $Hg(As_2O_6)$ (Weil, 2000); As_2O_5 (Jansen, 1978); $AsPO_5$ (Jansen *et al.*, 1992). The As—O distances in the structures available in the ICSD were directly calculated using ICSD software; only $Na_2As_4O_{11}$ (Driss, Jouini & Omezzine, 1988) showed inconsistencies. The bond lengths in the paper differ considerably from that of the ICSD, which is astonishing since the atomic coordinates are identical in both instances (obviously there must be some error in the atomic coordinates given in the paper) – therefore the distances given in the paper were used for analysis.

The mean As—O distance in these 33 polyhedra is 1.830 (2) Å. The distances range between 1.736 and 1.918 Å for individual As—O distances and from 1.811 to 1.857 Å for average distances of the 33 individual polyhedra. This is somewhat shorter than expected as it gives a mean BVS of 5.08 (2) v.u. for all used AsO_6 octahedra. A thorough discussion of all AsO_4 and AsO_6 polyhedra in inorganic arsenate compounds will be published separately (Schwendtner, 2007).

4. Conclusions

AsO_6 is a very uncommon coordination polyhedron in As^V compounds, but compared with other As^V-bearing compounds it is rather common among M^+ arsenates and to a lesser extent among M^{2+} arsenates.

More than 20% of all AsO_6-bearing compounds (R < 0.08) are described in this paper for the first time. All of them were synthesized under mild hydrothermal conditions without added water (basically from a melt of arsenic acid). All the compounds listed in Table 1 were also grown by relatively mild conditions between 773 K ($AgAsO_3$; Curda *et al.*, 2004) and room temperature ($Ag_4H_4AsO_{14}$; Boudjada & Averbuch-Pouchot, 1984). As with the new compounds the absence of H_2O (Curda *et al.*, 2004) was noted to be crucial. This might suggest that the more prevalent high-temperature solid-state reactions or hydrothermal conditions containing H_2O are less suited for the growth of AsO_6-bearing compounds, although high-temperature synthesis (chemical transport reaction at 993 K) has been successful in the case of $Cd(As_2O_6)$ (Weil, 2001) for example. In general, high coordination numbers seem to be less common at higher temperatures. Therefore, the number of octahedrally coordinated As atoms is likely to increase significantly if the following two conditions are adhered to during synthesis: mild temperatures and high concentration of arsenic (no dilution with H_2O).

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