A view of the structure of Nb$_2$Se$_9$ is given in Fig. 2. The structure is comprised of one-dimensional chains that run along the *c* axis. The chains contain Nb atoms in bicapped trigonal prisms of Se atoms. The trigonal prisms are linked through a quadrilateral face to one prism and through an edge and a capping atom to a second prism. The sharing of a quadrilateral face allows for the formation of a short Nb—Nb distance [2·895 (2) Å]. This distance is similar to the value 2·871 (4) Å, found in the structurally related compound NbS$_2$Cl$_2$ (Rijnsdorp, de Lange & Wieger, 1979). In addition to this short Nb—Nb distance a variety of Se—Se bonds are also present in the structure. The quadrilateral face is formed by two pairs of Se atoms [Se—Se = 2·319 (2) and 2·316 (2) Å] while the other end of the trigonal prism contains an Se$_5$ unit. This Se$_5$ unit contains two short Se—Se bonds [2·365 (2) and 2·364 (2) Å] and two longer Se—Se distances [2·643 (2) and 2·663 (2) Å]. The bond distances and bond angles reported here, while perhaps ten times more precise, do not differ significantly from those reported earlier [*e.g.* Se(1)—Se(8) = 2·365 (2) Å *versus* 2·34 (3) Å]. The description of the structure in valence terms as $2\mathrm{Nb}^{4+}2(\mathrm{Se}_2)^{2-}(\mathrm{Se}_5)^{4-}$ with an Nb—Nb bond is consistent with the observed semiconducting behavior (Rouxel, 1982).

The metal–metal bonding in both CuTaS$_3$ and Nb$_2$Se$_9$ and the Se—Se bonding in the latter compound are typical of ternary chalcogenides. As the structural phenomena in ternary chalcogenides are often linked to the physical properties a detailed knowledge of the metrical details of these compounds is of particular importance. The improved accuracy of the bond distances and angles in Nb$_2$Se$_9$ and CuTaS$_3$ will aid in characterizing metal–metal and chalcogen–chalcogen bonds in other compounds.

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Absolute Structure of LiH$_2$AsO$_4$

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Abstract. $M_r = 147·87$, orthorhombic, $Pna2_1$, $a = 6·416$ (2), $b = 7·727$ (3), $c = 7·298$ (2) Å, $V = 361·8$ Å^3, $Z = 4$, $D_x = 2·72$ g cm^{-3}, $\lambda(\mathrm{Ag}\ K\alpha) = 0·5608$ Å, $\mu = 5·14$ cm^{-1}, $F(000) = 280$, $T = 293$ K. Final $R = 0·018$ for 1700 unique observed reflections. The absolute crystal structure has been solved. LiH$_2$AsO$_4$ is isostructural with LiH$_2$PO$_4$, but one of the two independent hydrogen bonds (these bonds involve the

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same O atoms in the two compounds) is different: the O(4)—H(2)···O(2) bond in the phosphate becomes O(4)···H(2)—O(2) in the arsenate.

Introduction. A systematic study of MH_2PO_4 and MH_2AsO_4 crystal structures (M = Li, Na, K, NH_4, Rb, Cs, Hg, Ag, Tl) has been carried out by one of us (Boudjada, 1983). It appears that the monophosphate is isostructural with the corresponding monoarsenate when the two compounds exist. However, one exception for M = Li was reported in the literature: LiH_2AsO_4 was found to be monoclinic (Rémy & Bachet, 1967) but no crystal structure was reported, and the crystal structure of LiH_2PO_4 has been solved with the $Pna2_1$ space group (Catti & Ivaldi, 1977). Recently we have synthesized LiH_2AsO_4 which has unit-cell parameters very close to those of LiH_2PO_4.

Thus, it was interesting to know the crystal structure of LiH_2AsO_4 in order to compare it with that of LiH_2PO_4 and to verify whether the two compounds have the same hydrogen bonds.

Experimental. Crystals were prepared by mixing concentrated solutions of arsenic acid and pure hydrated lithium hydroxide in proportion given by the lithium arsenate phase diagram (Rémy & Guérin, 1963). The crystals are hygroscopic but did not deteriorate during the measurement time. Preliminary precession photographs showed the crystals to belong to the orthorhombic space group $Pna2_1$ or *Pnam*.

Spherical crystal with 130 μm radius, mounted at random on a Philips PW 1100 four-circle diffractometer; graphite-monochromated Ag $K\alpha$ radiation, ω–2θ scan mode, scan width (1·5 + 0·4 tgθ)°, scan speed 0·06° s^{-1}; lattice parameters obtained by averaging 32 orientation matrices from data collection; three standard reflections checked every 2 h, no variation in intensity; 4309 reflections collected in the whole Ewald sphere for $2 \leq \theta \leq 21°$ and in a quarter of the sphere for $21 \leq \theta \leq 30°$ (h −11→9, k −13→11, l ±12). Lorentz–polarization correction made. The average of equivalent reflections with respect to the $Pna2_1$ symmetry gave a final set of 1913 unique observations with $R_{\rm int}$ = 0·025 $(=\sum|F_{oi}^2 - F_{{\rm ave}i}^2|/\sum F_{oi}^2$ with $F_{{\rm ave}i}$ being the average value of all F_o in the set of equivalent reflections which contains the ith one). 213 sets of equivalent reflections with an R factor greater than 0·1 (= $4R_{\rm int}$) were manually removed; they correspond to absent or weak reflections. No absorption correction was performed.

As and O atomic positions were taken from the LiH_2PO_4 structure (Catti & Ivaldi, 1977), in agreement with the Patterson map. Li atomic positions were found from difference Fourier maps. Full-matrix least-squares refinements based on F with 777 low-order reflections and anisotropic temperature factors converged to wR = 0·032. The origin along z is fixed by the As atoms [z = 0·17317 for easy comparison with Catti & Ivaldi (1977)]. Unit weights.

Table 1. *Atomic coordinates and isotropic thermal factors with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	$B_{\rm eq}$(Å^2)
As	0·30199 (3)	0·42074 (2)	0·17317	0·982 (9)
O(1)	0·2796 (3)	0·3141 (2)	0·3676 (2)	1·395 (5)
O(2)	0·4218 (3)	0·6172 (2)	0·1998 (2)	1·734 (6)
O(3)	0·0612 (3)	0·4887 (2)	0·0956 (3)	1·397 (6)
O(4)	0·4216 (3)	0·3093 (2)	0·0098 (2)	1·706 (6)
Li	0·4835 (8)	0·7847 (6)	−0·0001 (6)	1·427 (12)
H(1)	−0·009 (10)	0·359 (8)	0·034 (8)	8·09 (1·5)
H(2)	0·473 (9)	0·632 (7)	0·296 (9)	6·66 (1·5)

By changing the z coordinate of all atoms into $\frac{1}{2}-z$ (this operation is equivalent to a symmetry center), the refinement converged to wR = 0·023, giving the absolute configuration of LiH_2AsO_4: the F_o and F_c of the hkl, $hk\bar{l}$ pair are now in better agreement. Subsequently the H atoms were located on difference Fourier maps after extinction correction: Gaussian angular distribution (η = 0·65″), size distribution negligible (Becker & Coppens, 1975).

In final cycle: R = 0·018, wR = 0·019, S = 0·2 with 1700 observations.* $(\Delta/\sigma)_{\rm max}$ = 1·2 for z coordinate of H(1). Final difference map showed residual electron density (max. = 1·3, min. = −0·9 e Å^{-3}) near As atoms.

The *SDP* package (Enraf–Nonius, 1979) installed on a PDP11/70 was used for initial refinements; final refinements with extinction correction were carried out with *LINEX* (Coppens, 1974) on a CDC6400. Atomic scattering form factors from Fukamachi (1971) for As, O, Li; from Stewart, Davidson & Simpson (1965) for H; anomalous-dispersion factors f' and f'' from Cromer & Liberman (1970). The final atomic parameters are given in Table 1.

Discussion. LiH_2AsO_4 was found to be monoclinic (β = 90°32′) pseudo-orthorhombic by Rémy & Bachet (1967). The density they measured (2·75 g cm^{-3}) is close to that calculated for the orthorhombic form (2·72 g cm^{-3}). Nevertheless the volume of the monoclinic Rémy & Bachet (1967) cell is nearly twice that of the orthorhombic cell, 708·2 and 361·8 Å^3, respectively, and we found no relation between the two unit cells. The methods used by Rémy & Bachet (1967) (Weissenberg, rotation and Laue photographs on single

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43748 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	LiH_2AsO_4*		LiH_2PO_4†
As—O(1)	1·647 (3)	P—O(1)	1·500 (1)
As—O(2)	1·712 (3)	P—O(2)	1·503 (1)
As—O(3)	1·727 (3)	P—O(3)	1·596 (1)
As—O(4)	1·659 (3)	P—O(4)	1·577 (1)
Average	1·686 (3)		1·577 (1)
Li—O(1)	1·956 (5)		1·956 (3)
Li—O(1)′	1·957 (5)		1·945 (3)
Li—O(2)	1·990 (5)		1·945 (3)
Li—O(3)	1·950 (5)		1·982 (3)
Average	1·963 (5)		1·957 (3)

* This work.
† Catti & Ivaldi (1977).

crystals and powder patterns) are reliable for cell and space-group determination. Thus it seems that LiH_2AsO_4 may have two phases.

The structure reveals infinite chains along [100] of corner-sharing LiO_4 tetrahedra at about $y = \frac{1}{4}$, $z = \frac{1}{2}$ and $y = \frac{3}{4}$, $z = 0$. These chains are linked by AsO_4 tetrahedra forming a three-dimensional framework of tetrahedra. If H atoms are not taken into account, LiH_2AsO_4 has the same structure as LiH_2PO_4 (Catti & Ivaldi, 1977). The average Li—O distance (1·963 Å) of the LiO_4 tetrahedra is very close to that in LiH_2PO_4 (1·957 Å) as indicated in Table 2. The AsO_4 tetrahedra present two long distances (1·712 and 1·727 Å) and two short ones (1·647 and 1·659 Å) with an average of 1·686 Å: a similar distortion occurs in LiH_2PO_4. The same results are obtained in AgH_2AsO_4 (Boudjada, 1983) although this last compound is not isostructural with LiH_2AsO_4 (1·719 and 1·721 Å for the two long distances; 1·655 and 1·653 Å for the two short ones).

Fig. 1(*a*) shows the hydrogen bonds in LiH_2AsO_4. H(1) is at the same position between O(3) and O(4) in the two compounds, but H(2) is transferred from O(4) in the arsenate to O(2) in the phosphate (Fig. 1*b*). This is confirmed by the distances in the AsO_4 and PO_4 tetrahedra: the two short distances correspond to the As—O (or P—O) bonds and the two long ones to the As—O—H (or P—O—H) bonds (Table 3). Thus, in the arsenate the donor atoms for hydrogen bonds are O(3) and O(2), whereas they are O(3) and O(4) in the phosphate [in fact O(4) is both acceptor and donor in the phosphate]. The O(3)···O(4) distances are the shortest O—O distances in the two compounds.

The large H thermal vibrations (6·7 and 8·1 Å^2) suggested the possibility of high mobility of H atoms in LiH_2AsO_4. However, conductivity measurements using the experimental set-up of a complex impedance method (Delabouglisse, 1981) did not indicate a good protonic conduction: 10^{-6} and $10^{-7}\ \Omega^{-1}\ cm^{-1}$ with powder and crystal, respectively.

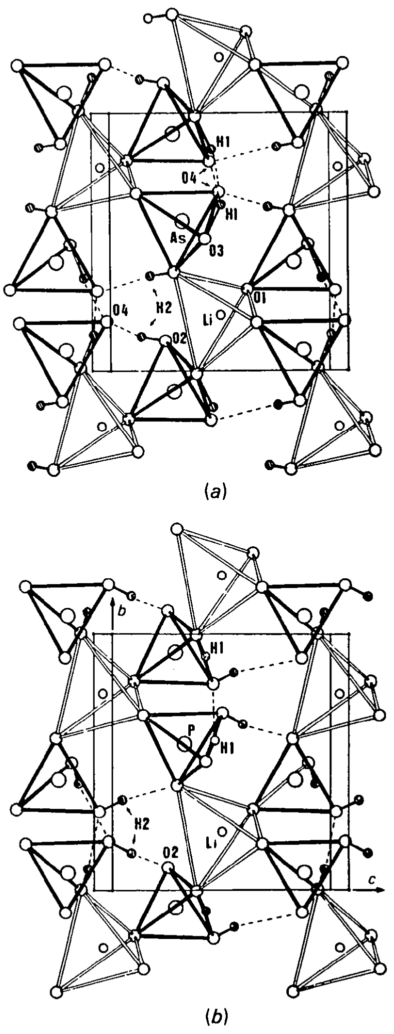

Fig. 1. Hydrogen bonds in (*a*) LiH_2AsO_4 and (*b*) LiH_2PO_4. Projection on the *xy* plane of the figure: *c* rotated by 5° around $y = b$.

Table 3. *Interatomic distances* (Å) *and angles* (°) *in hydrogen bonds* (*with e.s.d.'s in parentheses*) *in* LiH_2AsO_4 *compared with those in* LiH_2PO_4 (*Catti & Ivaldi*, 1977)

	As—O(3)—H(1)···O(4)	P—O(3)—H(1)···O(4)	As—O(2)—H(2)···O(4)	P—O(4)—H(2)···O(2)
O···O	2·549 (4)	2·684 (2)	2·540 (4)	2·564 (1)
O—H	1·19 (2)	0·78 (3)	0·78 (2)	0·80 (4)
H···O	1·39 (2)	1·91 (3)	1·76 (2)	1·76 (4)
O—H···O	164 (1)	171 (3)	173 (2)	169 (3)
As(or P)—O—H	102 (1)	107 (2)	115 (1)	118 (2)
As(or P)—O···O	96·9 (1)	100·5 (1)	118·5 (1)	125·8 (1)

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Die Struktur des Monoklinen Tetranatriumdivanadathydrats

VON KATSUO KATO UND EIJI TAKAYAMA-MUROMACHI

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Abstract. $Na_4V_2O_7.H_2O$ (mon.), $M_r = 323\cdot85$, monoclinic, $P2_1/c$, $a = 8\cdot4367$ (4), $b = 8\cdot6641$ (6), $c = 11\cdot2554$ (9) Å, $\beta = 95\cdot161$ (7)°, $V = 819\cdot4$ (1) Å^3, $Z = 4$, $D_x = 2\cdot625$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha_1) = 1\cdot540562$, $\lambda(\mathrm{Cu}\,K\alpha_2) = 1\cdot544390$ Å for lattice parameters, $\lambda(\mathrm{Mo}\,K\bar{\alpha}) = 0\cdot71073$ Å for intensity measurement, $\mu = 2\cdot42$ mm^{-1}, $F(000) = 624$, $T = 298$ K, final $R = 0\cdot054$ for 2059 unique observed reflections. The V_2O_7 group has a nearly eclipsed conformation with V—O—V angle 126·1 (2)°. The V_2O_7 groups and water molecules are arranged in layers parallel to (102), and the layers are stacked with a translation of [100]. The Na^+ ions are situated between the layers and surrounded by five or six O atoms. The structure is closely related to that of the triclinic modification [Kato & Takayama-Muromachi (1985). *Acta Cryst.* C**41**, 1411–1413].

Einleitung. Von dem dimorphen $Na_4V_2O_7.H_2O$ ist die Struktur der triklinen Modifikation bereits von uns bestimmt worden (Kato & Takayama-Muromachi, 1985). Die Struktur der anderen, monoklinen Modifikation wird in der vorliegenden Arbeit beschrieben und mit derjenigen der triklinen verglichen. Zwischen den beiden Strukturen besteht eine große Ähnlichkeit, die jedoch erst dann zum Vorschein kommt, wenn man für die trikline Modifikation eine neue Aufstellung wählt, die sich auf die konventionelle in der Literatur wie folgt bezieht: $\mathbf{a}' = -\mathbf{c}$, $\mathbf{b}' = -\mathbf{a}+\mathbf{b}$, $\mathbf{c}' = \mathbf{a}+\mathbf{b}$. Die neue Raumgruppe ist $A\bar{1}$, die Gitterparameter errechnen sich zu $a' = 8{,}313$, $b' = 8{,}787$, $c' = 11{,}369$ Å, $\alpha' = 86{,}35$, $\beta' = 95{,}63$ und $\gamma' = 90{,}48°$, $Z = 4$. Im folgenden wird auf diese Aufstellung Bezug genommen.

Experimentelles. Kristall aus wässeriger Lösung bei 393 K, Gestalt unregelmäßig, Größe 0,05 × 0,1 × 0,3 mm, hygroskopisch, eingeschlossen in Glaskapillare mit Wandstärke 0,01 mm. Gitterparameter aus 2θ-Werten ($2\theta > 90°$) von 22 $h0l$- und 25 $hk0$-Reflexen gemessen auf Rückstrahl-Weissenberg-Aufnahmen mit Filmradius 57,3 mm. Intensitäten von 3796 Reflexen mit $h\,0\rightarrow13$, $k\,0\rightarrow13$, $l\,-18\rightarrow18$ und bis zu $(\sin\theta)/\lambda = 0{,}807$ Å^{-1} gemessen auf dem Einkristalldiffraktometer AFC-3 der Fa. Rigaku, ω-Abtastung für $2\theta < 30°$, $\omega/2\theta$-Abtastung für $2\theta \geq 30°$, Abtastbreite und -geschwindigkeit $1{,}1° + 0{,}5°\tan\theta$ bzw. 2° min^{-1} für ω-Kreis. Vier Standardreflexe, Standardabweichungen ihrer Strukturamplituden 0,5%. 1730 schwache Reflexe mit $I \leq \sigma(I)$ als unbeobachtet betrachtet, 2066 Reflexe beobachtet, davon 2059 unabhängig. Keine Absorptionskorrektur. Struktur gelöst mit Hilfe der Pattersonfunktion, H-Atome nicht lokalisiert. Atomkoordinaten, anisotrope Temperaturfaktoren,[†] ein Skalierungsfaktor (s) für die Strukturamplituden sowie ein freier Parameter (g) für Extinktionskorrektur verfeinert nach der Methode der kleinsten Quadrate bezüglich F, $R = 0{,}054$, $wR = 0{,}036$, $S = 1{,}46$, Wichtung der Strukturamplituden nach $\sigma(F)$. Atomformfaktoren nach Cromer & Mann (1968), Dispersionskorrekturen nach Cromer & Liberman (1970). Extinktionskorrektur nach Zachariasen (1967, 1968) unter Verwendung einer ver-

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[†] Die Liste der Strukturamplituden und die Tabelle der anisotropen Temperaturfaktoren sind beim British Library Document Supply Centre (Supplementary Publication No. SUP 43696: 22 pp.) hinterlegt. Kopien sind erhältlich durch: The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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