L'assemblage de ces polyèdres constitue un feuillet parallèle au plan *ab*. La jonction entre ces feuillets qui se développe à la cote moyenne $z = 0$ parallèlement au plan (001) est assurée par des liaisons par pont hydrogène. La présence de ces dernières au sein de la structure est évidente, elles ont été localisées à partir des positions des atomes d'hydrogène déterminées grâce aux dernières cartes de densité électronique. L'existence de ces liaisons est par ailleurs confirmée par la faible distance entre atomes d'oxygène donneurs et accepteurs mais aussi par le fort décalage des bandes d'absorption des groupements OH enregistrées sur le spectre infra-rouge.

Dans le Tableau 3 ont été rassemblées les principales informations concernant ces liaisons hydrogène. Ce tableau comporte en outre des indications sur la contribution de ces liaisons hydrogène dans la cohésion de l'édifice structural. On s'aperçoit que seulement le tiers des liaisons hydrogène participe à jonction inter-feuillets, les deux tiers restants sont des liaisons intra-feuillets et servent à la consolidation propre du feuillet (Fig. 2). Parmi les trois atomes d'hydrogène participant à des liaisons inter-feuillets: H'(O*w*2) et H'(O*w*1) proviennent de molécules d'eau; l'une de ces liaisons est assez forte: O*w*(2)—O(9) = 2,70 Å; H(O12) qui appartient à l'anion [P(3)O$_3$(OH)] engendre une liaison par pont particulièrement forte puisque O(11)—O(12) = 2,63 Å. On peut donc considérer que ces liaisons par pont assurent une bonne jonction entre les feuillets. Les autres liaisons par pont hydrogène jouent un rôle important dans la consolidation du feuillet notamment dans les zones moins compactes situées en lisière du feuillet; c'est le cas en particulier des liaisons générées à partir de H(O7), H''(O*w*1) et H''(O*w*2).

Parmi les liaisons par pont hydrogène intra-feuillets il en existe deux: O(7)—H(O7)···O(11) et O(6)—H(O6)···O(10) exceptionnellement fortes puisque O(7)—O(11) = 2,54 Å et O(6)—O(10) = 2,58 Å. Ces liaisons jouent un rôle particulier puisqu'elles réalisent un pontage entre les trois groupements anioniques indépendants HPO$_4^{2-}$, il existe donc au sein de cette structure un regroupement priviligié des trois hydrogénophosphates, qui compte tenu de la force des liaisons hydrogène se rapproche d'un trimère anionique de formule [H$_3$P$_3$O$_{12}$]$^{6-}$.

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The Pseudo-orthorhombic Structure of Caesium Dihydrogendecavanadate Tetrahydrate

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Abstract. Cs$_4$H$_2$V$_{10}$O$_{28}$.4H$_2$O, $M_r = 1581\cdot1$, monoclinic, $P2_1/c$, $a = 10\cdot072\ (4)$, $b = 14\cdot077\ (3)$, $c = 11\cdot528\ (3)$ Å, $\beta = 108\cdot10\ (3)°$, $V = 1554\ (2)$ Å^3, $Z = 2$, $D_x = 3\cdot38$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 7\cdot8$ mm^{-1}, $F(000) = 1452$, $T = 298\ (2)$ K, $R = 7\cdot5$, $wR = 7\cdot8$% for 1133 reflections with $I > 3\sigma(I)$. The (H$_2$V$_{10}$O$_{28}$)$^{4-}$ anion is sited on a symmetry centre and displays approximate point symmetry *mmm* with one of the local twofold axes parallel to the **c** direction. This gives rise to orthorhombic pseudo-symmetry which can be described in terms of the unit cell 4**a** + **c**, **b**, **c**. Packing considerations show that a 2*Or* polytype obtained through cell twinning of the monoclinic cell by 180° rotation about the *c* axis is not forbidden by steric

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constraints. A very short intermolecular O–O distance [2·59 (3) Å] between neighbouring $(H_2V_{10}O_{28})^{4-}$ anions is indicative of a strong hydrogen bond which permits the approximate location of the proton sites. The structure is built up from layers of $(H_2V_{10}O_{28})^{4-}$ anions perpendicular to **a***; within each layer the $(H_2V_{10}O_{28})^{4-}$ anions are stabilized by a net of hydrogen bonds; the V–O bond distances range between 1·57 (2) and 2·34 (2) Å.

Introduction. The present study was undertaken with the twofold aim of determining the protonation sites in the $(H_2V_{10}O_{28})^{4-}$ decavanadate anion and to help in the interpretation of the dehydration mechanism of the title compound. The former problem is of interest because the basic oxygen sites in metal–oxygen compounds are directly related to their reactivity and possible reaction pathways. With regard to the second problem, the interest arises because the dehydration behaviour of this salt is strikingly different from those of other decavanadates. The reaction is reversible without appreciable thermolysis of the anion, in contrast to the situation in other decavanadates which are known to be destroyed by heating after the loss of a certain number of water molecules (depending upon the bonding properties of the cation). This reaction, which leads to lower condensed vanadates and oxides of vanadium (Ulicka, 1980; Ulicka & Zúrkova, 1981), shows the stabilizing role of water of crystallization in crystalline decavanadate hydrates. [However, the existence of zinc and magnesium anhydrous decavanadates with relatively high thermal stability has been reported (Ulicka, 1980).] We have observed that controlled thermal dehydration of the compound leads to an anhydrous non-crystalline solid, which in the presence of water vapour, turns back to the original crystalline hydrate. The study of the hydration kinetics in the solid state, in connection with the stabilizing role of protons in the structure, is the purpose of future work.

Experimental. Bright-orange crystalline hexagonal plates obtained as described elsewhere (Jahr & Preuss, 1965) were grown at 298 (2) K and kindly forwarded to us by Dr E. J. Baran. Lattice parameters and space group were first determined by Weissenberg and precession photographs. Space-group determination was complicated by the pseudo-orthorhombic symmetry displayed by the reciprocal lattice. A crystal of irregular shape, 0·25 × 0·20 × 0·30 mm, was mounted on a Nonius CAD-4 diffractometer. 3030 reflections were collected using graphite-monochromated Mo $K\alpha$ radiation, from which 2241 were independent, excluding all $hk0$ (see below); $R_{\rm int} = 0{\cdot}06$. Cell parameters were obtained from 25 reflections with $10 < \theta < 18°$; ω–2θ scans were used, scan width $(0{\cdot}75 + 0{\cdot}35\tan\theta)°$, max. scan speed 10° min^{-1}; range of hkl: $-12 < h < 12$, $k < 17$, $l < 14$, $\theta_{\max} = 25°$. Standards $4\bar{6}0$, 006 and 080 varied ±1·6% of mean intensities over data collection. Lorentz, polarization and extinction corrections were applied. The caesium atoms were located from a Patterson map and all other non-H atoms by alternate cycles of isotropic least squares and difference maps. The structure was refined from 1133 reflections with $I > 3\sigma(I)$; the $hk0$ reflections were contaminated by twinning and therefore not included in the refinement. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o) + 0{\cdot}00233F_o^2]^{-1}$. The Cs and V atoms were treated anisotropically; the total number of parameters was 129. Extinction correction was performed by using $F_{\rm corr} = F_c/[1 - 10^{-8}\,\chi|F_c|^2/\sin\theta]$, where χ refined to 5·7. Refinement was stopped when max. $\Delta/\sigma = 0{\cdot}005$; $S = 1{\cdot}25$; at this stage $R = 0{\cdot}075$ and $wR = 0{\cdot}078$. A final difference map showed $\Delta\rho$ fluctuations within ±2·2 e Å^{-3} at a distance of less than 1 Å from the Cs atoms. These fluctuations and the rather high R-factor values are probably due to the combined effects of twin contamination and uncorrected absorption. Scattering form factors were taken from Cromer & Mann (1968) and corrections for anomalous dispersion from Cromer & Liberman (1970). Most calculations were performed with *SHELX76* (Sheldrick, 1976) on a VAX 11/780 computer.*

Discussion. Crystals are elongated plates of hexagonal shape with [001] along the elongation direction and [010] perpendicular to the longest edge, both in the plane of the plate. Weissenberg hkn ($n = 1,2,\ldots$) reciprocal layers and oscillation photographs of a crystal mounted along [001] displayed almost orthorhombic symmetry with no conventional extinction conditions. An appropriate (pseudo) orthorhombic unit cell was defined by the base vectors 4**a** + **c**, **b**, **c**, giving the cell constants $a' = 38{\cdot}307$, $b' = 14{\cdot}077$, $c' = 11{\cdot}528$ Å, $\beta = 91{\cdot}48°$, $\alpha = \gamma = 90°$. In terms of this cell, the conditions for possible reflections are $h = 4n + 4$, $k,l = 4n$; $h = 4n + 1$, $k,l = 4n + 1$; $h = 4n + 2$, $k,l = 4n + 2$; $h = 4n + 3$, $k,l = 4n + 3$; with $n = 0, \pm1, \pm2, \ldots$

Pseudo-symmetry occurs because the decavanadate polyanion (together with the four Cs atoms) displays approximate local point symmetry *mmm* and is orientated with one of its twofold axes approximately along **c**. To test quantitatively this situation, we compared the decavanadate polyanion with its equivalent obtained by a 180° rotation about an axis parallel to **c** by the method of Kabash (1976); the least-squares orthogonal matrix relating the two sets of homologous vectors was essentially the unit matrix and the

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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 43392 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

corresponding root-mean-square distance between homologous atoms was 0·01 Å.

Fig. 1 is a perspective projection of the decavanadate polyanion showing the system of nomenclature. Final atomic positions and equivalent isotropic temperature factors are given in Table 1. Interatomic distances and angles within the polyanion show that its geometry is similar to that found in all previously reported molecular structures for decavanadate salts (Evans, 1966; Swallow, Ahmed & Barnes, 1966; Saf'yanov & Belov, 1976; Saf'yanov, Kuz'min & Belov, 1978; Durif, Averbuch-Pouchot & Guitel, 1980; Debaerdemaeker, Arrieta & Amigo, 1982; Rivero, Rigotti, Punte & Navaza, 1984; Rivero, Punte, Rigotti & Navaza, 1985, 1987), Table 2. The decavanadate anion can be described as a section of cubic close-packed O atoms with V atoms in the distorted octahedral holes. The intrinsic approximate symmetry is *mmm*. Least-squares best planes for the assumed symmetry planes gave dihedral angles of 92·5 (1), 88·5 (1), 88·5 (1) and 91·1 (1)°; χ^2 values $[\sum(\Delta/\sigma^2)]$ were 21·7, 35·7 and 0·0. Table 2 gives V—O distances in the polyanion.

The coordination polyhedra around the Cs atoms are quite different and ill defined in shape. For that reason, we used the (arbitrary) criterion of defining the Cs environment inside a sphere of radus 3·5 Å. [Properly speaking the Cs—O coordination distance should be about 2·9 Å (Wells, 1975).] Cs(1) is coordinated to eight O atoms of neighbouring $(V_{10}O_{28})^{6-}$ anions and one water oxygen, O(*W*2). Its coordination number is therefore nine and the Cs—O distances range between 3·08 (2) and 3·38 (3) Å. Cs(2) is eight-coordinated to six decavanadate O atoms and the two water molecules. In this case Cs—O distances range between 3·09 (2) and 3·41 (2) Å.

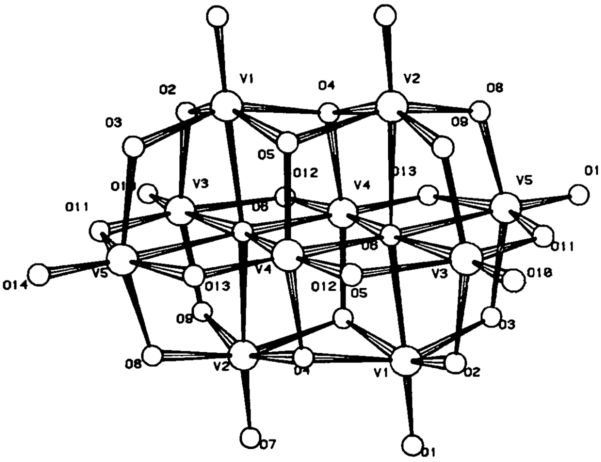

Fig. 1. Perspective projection of the decavanadate polyanion showing the system of nomenclature.

Table 1. *Fractional atomic coordinates and isotropic temperature factors* (Å²)

For Cs and V atoms, the equivalent isotropic temperature factor was calculated from the anisotropic *B*'s using $B = \frac{4}{3}\sum_{ij}B_{ij}(\mathbf{a}_i.\mathbf{a}_j)$.

	x	*y*	*z*	$B_{eq/iso}$
V(1)	0·3152 (6)	0·3988 (4)	0·5765 (4)	1·2 (1)
V(2)	0·3337 (6)	0·3887 (4)	0·3215 (4)	1·4 (2)
V(3)	0·3801 (6)	0·5860 (4)	0·7268 (5)	1·9 (2)
V(4)	0·3899 (6)	0·5869 (3)	0·4636 (5)	1·3 (1)
V(5)	0·6028 (6)	0·4298 (4)	0·7964 (4)	1·5 (2)
Cs(1)	0·3160 (3)	0·1310 (2)	0·4538 (2)	2·86 (7)
Cs(2)	0·0718 (3)	0·7674 (2)	0·3992 (3)	3·67 (8)
O(1)	0·198 (2)	0·320 (2)	0·544 (2)	2·4 (4)
O(2)	0·252 (2)	0·484 (1)	0·660 (2)	1·0 (3)
O(3)	0·443 (2)	0·344 (2)	0·722 (2)	1·6 (4)
O(4)	0·271 (2)	0·473 (1)	0·431 (2)	1·4 (4)
O(5)	0·443 (2)	0·342 (1)	0·486 (2)	1·0 (3)
O(6)	0·495 (2)	0·499 (1)	0·614 (2)	1·0 (3)
O(7)	0·216 (2)	0·312 (2)	0·288 (2)	1·7 (4)
O(8)	0·272 (2)	0·477 (2)	0·197 (2)	1·7 (4)
O(9)	0·462 (2)	0·338 (2)	0·258 (2)	1·5 (4)
O(10)	0·292 (3)	0·647 (2)	0·790 (2)	3·2 (5)
O(11)	0·485 (2)	0·505 (2)	0·844 (2)	1·8 (4)
O(12)	0·312 (2)	0·638 (2)	0·559 (2)	1·8 (4)
O(13)	0·684 (2)	0·366 (2)	0·675 (2)	1·6 (4)
O(14)	0·677 (3)	0·369 (2)	0·913 (2)	3·2 (5)
O(*W*1)	−0·003 (4)	0·053 (3)	0·182 (3)	8· (1)
O(*W*2)	−0·002 (7)	0·577 (5)	0·082 (5)	15· (1)

Table 2. *Interatomic distances* (Å) *and angles* (°) *in the decavanadate polyanion*

Diagonal terms terms are V—O distances, upper diagonal terms O—O distances and lower diagonal ones O—V—O angles. Notation is identical to that of Rivero *et al.* (1984).

	V_{I}	O*g*	O*d*′	O*d*	O*b*′	O*b*	O*a*
	V(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O*g*	O(1)	1·58 (3)	2·64 (3)	2·70 (3)	2·73 (3)	2·77 (3)	3·80 (3)
O*d*′	O(2)	104· (1)	1·78 (2)	2·69 (3)	2·71 (3)	3·76 (3)	2·67 (3)
O*d*	O(3)	100· (1)	93·1 (9)	1·93 (2)	3·73 (3)	2·72 (3)	2·64 (3)
O*b*′	O(4)	103· (1)	98·7 (9)	153·3 (9)	1·91 (2)	2·47 (3)	2·60 (3)
O*b*	O(5)	98· (1)	157·7 (9)	86·1 (8)	77·3 (8)	2·05 (2)	2·62 (3)
O*a*	O(6)	174· (1)	82·8 (8)	78·6 (8)	74·7 (8)	75·2 (7)	2·23 (2)

	V_{I}	O*b*′	O*b*	O*a*	O*g*	O*d*′	O*d*
	V(2)	O(4)	O(5)	O(6′)	O(7)	O(8)	O(9)
O*b*′	O(4)	1·97 (2)	2·47 (3)	2·60 (3)	2·76 (8)	2·695 (6)	3·70 (3)
O*b*	O(5)	77·3 (8)	1·99 (2)	2·62 (3)	2·72 (3)	3·76 (3)	2·69 (3)
O*a*	O(6′)	77·2 (8)	77·3 (7)	2·29 (2)	3·65 (3)	2·68 (3)	2·69 (3)
O*g*	O(7)	102· (1)	99· (1)	175· (1)	1·56 (2)	2·68 (3)	2·63 (3)
O*d*′	O(8)	89·7 (9)	156·1 (9)	80·0 (8)	103· (1)	1·85 (2)	2·67 (3)
O*d*	O(9)	154·5 (9)	90·1 (9)	81·0 (8)	102· (1)	93· (1)	1·82 (2)

	V_{II}	O*d*	O*a*	O*d*	O*f*	O*c*	O*e*
	V(3)	O(2)	O(6)	O(9′)	O(10)	O(11)	O(12)
O*d*	O(2)	1·92 (2)	2·67 (3)	3·71 (3)	2·70 (3)	2·65 (3)	2·62 (3)
O*a*	O(6)	76·9 (8)	2·34 (2)	2·69 (3)	3·90 (3)	2·69 (3)	2·63 (3)
O*d*	O(9′)	154·8 (9)	78·4 (8)	1·88 (2)	2·71 (4)	2·63 (3)	2·60 (3)
O*f*	O(10)	101· (1)	174· (1)	103· (1)	1·57 (3)	2·72 (3)	2·74 (3)
O*c*	O(11)	89·5 (9)	79·2 (8)	90·5 (9)	106· (1)	1·83 (2)	3·71 (3)
O*e*	O(12)	84·2 (9)	74·4 (8)	84·7 (9)	100· (1)	154· (1)	1·98 (2)

	V_{III}	O*b*	O*b*′	O*a*	O*a*′	O*e*	O*e*′
	V(4)	O(4)	O(5′)	O(6)	O(6′)	O(12)	O(13′)
O*b*	O(4)	1·97 (2)	3·78 (3)	2·59 (3)	2·60 (3)	2·71 (3)	2·68 (3)
O*b*′	O(5′)	157·3 (9)	1·89 (2)	2·62 (3)	2·68 (3)	2·69 (3)	2·73 (3)
O*a*	O(6)	78·5 (8)	82·9 (8)	2·12 (2)	2·66 (2)	2·63 (3)	3·77 (3)
O*a*′	O(6′)	80·2 (8)	83·5 (8)	78·9 (7)	2·13 (2)	3·73 (3)	2·61 (3)
O*e*	O(12)	95· (1)	97· (1)	86·1 (9)	165· (1)	1·70 (2)	2·71 (3)
O*e*′	O(13′)	94· (1)	100· (1)	165·8 (9)	87·8 (9)	107· (1)	1·68 (2)

	V_{II}	O*d*	O*a*	O*d*	O*c*	O*e*	O*f*
	V(5)	O(3)	O(6)	O(8′)	O(11)	O(13)	O(14)
O*d*	O(3)	1·98 (2)	2·64 (3)	3·71 (3)	2·63 (3)	2·66 (3)	2·70 (3)
O*a*	O(6)	76·7 (8)	2·27 (2)	2·68 (3)	2·69 (3)	2·61 (3)	3·83 (3)
O*d*	O(8′)	158· (1)	81·6 (8)	1·80 (2)	2·65 (3)	2·62 (3)	2·64 (3)
O*c*	O(11)	88·1 (9)	81·9 (8)	94· (1)	1·80 (2)	3·75 (3)	2·66 (3)
O*e*	O(13)	83·1 (9)	74·4 (8)	85·7 (9)	156· (1)	2·04 (2)	2·77 (3)
O*f*	O(14)	98· (1)	172· (1)	103· (1)	104· (1)	99· (1)	1·57 (2)

Decavanadate polyanions are sited on symmetry centres with $x = \frac{1}{2} \pm n$, n integer, giving rise to infinite layers parallel to the *bc* planes and stacked along the **a** direction. Within these layers, each polyanion subtends four short intermolecular O–O contacts, all crystallographically equivalent, of 2·59 (3) Å. These are the only short intermolecular distances [the next shortest being 3·11 (3) Å] and are a strong indication of hydrogen bonding, in spite of the fact that protons could not be located from the maps. The O atoms involved in the interaction are the *d*-type (Evans, 1966) O(3) and O(9).

$(V_{10}O_{28})^{6-}$ and several other polyoxoanions of the early transition elements are protonated in solution and/or in the solid state. Klemperer & Shum (1977) and Howarth & Jarrold (1978) have determined the protonation sites of $(H_2V_{10}O_{28})^{4-}$ in solution using ^{17}O NMR and ^{51}V NMR spectroscopy, respectively. The former authors found that O*b* and O*d* type (see Table 2) are the most basic oxygens, O*b* being more basic than O*d*, while the latter authors pointed out that the most probable protonation sites are at the apical oxygens O*f* and O*g*. X-ray structural data on tetrakis-(4-ethylpyridinium) decavanadate (Debaerdemaeker, Arrieta & Amigo, 1982) agree with the results of Klemperer & Shum (1977), because the shortest distances [2·63 (2) and 2·73 (2) Å] between the pyridine N atom and the O atoms of the decavanadate ion are those involving O*b* and O*d* types. This compound, however, is not the most adequate for using its shortest hydrogen-bond lengths as indicative of O-atom basicity, because of the steric effects of a large group such as ethylpyridinium. In the present case, the rather short intermolecular distance between O(3) and O(9) and the fact that the second longest intermolecular O–O distance is 3·11 (3) Å are conclusive evidence that the protons are attached to those atoms.

The stabilizing role of the protons in the structure is indicated by thermal dehydration experiments. The dehydration process takes place in two steps: one corresponds to the loss of four water molecules (giving the anhydrous compound) and the other to the release of an additional water molecule resulting from the deprotonation of the polyanion, followed immediately by its total decomposition (Lavat, Baran & Escobar, 1983). The different dehydration behaviour of this compound compared with that in other decavanadates may be explained by the stabilizing intralayer character of the strong net of hydrogen bonds. It is reasonable to speculate that the layers are maintained after loss of the interlayer water molecules, thus preventing the structure from collapsing completely and allowing it to rebuild its three-dimensional order after recovering the interstitial water molecules. Fig. 2 is a stereoscopic projection of the structure showing the crystal packing and the net of hydrogen bonds.

The particular packing of the structure, which gives rise to the pseudo-orthorhombic symmetry described above, involves the question of whether true orthorhombic symmetry could eventually be realized by the compound. Although prediction of the occurrence of polytypism should be based on rigorous energy calculations, simple packing considerations may furnish useful information. A comparison with the monoclinic (1*M*) unit cell reported for potassium and rubidium hexacyanometallates (Kohn & Townes, 1961; Vannerberg, 1972, and references therein) shows that the ratios *a*/*c*, *b*/*c*, the monoclinic *β* angle and also the systematic extinctions are almost coincident with the equivalent parameters displayed by caesium dihydrogendecavanadate (0·84, 1·24 and 107·3° and 0·87, 1·22, 108·1°, respectively). Various different cells have been reported for the hexacyanometallates owing to the occurrence of different polytypes (particularly 1*M* and 2*Or* cells), with stacking vector ±**c**/4 and stacking direction along [100] and rotation about **c** (see Fig. 1 of Vannerberg, 1970). If by analogy we apply these rotation and stacking operations, they give rise to a displacement of one of the decavanadate layers with respect to the other by $\frac{1}{4}$ along [001]; as described above, these two layers are almost coincident by rotation about **c**. These considerations lead us to believe that existence of the 2*Or* cell is energetically possible although crystallization of the 1*M* polytype is more favourable in the experimental conditions reported.

Structure twinning, not resolved in the $l = 0$ reciprocal plane, is also observed. The macroscopic twin law relating one domain to the other is a mirror plane perpendicular to the [100] direction.

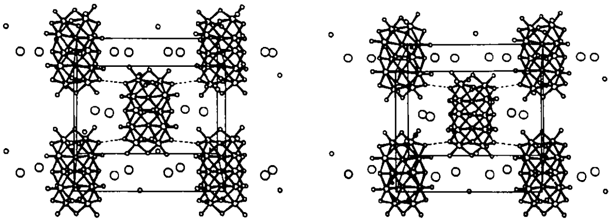

Fig. 2. Stereoscopic projection of the structure showing the crystal packing and the net of hydrogen bonds.

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Synthèse et Structure Cristalline de $LiInP_2O_7$

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Abstract. $M_r = 295\cdot7$, monoclinic, $P2_1$, $a = 7\cdot084$ (2), $b = 8\cdot436$ (2), $c = 4\cdot908$ (3) Å, $\beta = 110\cdot75$ (2)°, $V = 274\cdot3$ (1) Å^3, $Z = 2$, $D_x = 3\cdot58$ Mg m^{-3}, $F(000) = 276$, $\mu = 4\cdot76$ mm^{-1}, Ag $K\bar{\alpha}$, $\lambda = 0\cdot56085$ Å, room temperature, R factor 2·0% for 692 reflections. The structure of $LiInP_2O_7$ consists of InO_6 octahedra and pyrophosphate groups, P_2O_7. Each InO_6 group is connected, *via* In—O—P bonds, to five pyrophosphate groups: two corners of the InO_6 octahedra are linked to one P_2O_7 group and four others share corners with four distinct pyrophosphate groups. The lithium ion is located in the channel parallel to the c axis and is bonded to four oxygens of the $[InP_2O_7]$ framework with Li—O distances from 1·96 to 2·12 Å.

Introduction. Au cours de l'étude systématique des phases du système $Li_{1+x}Ti_{2-x}In_xP_3O_{12}$ présentant une conductivité ionique élevée (Hamdoune, Tranqui & Schouler, 1986) nous avons identifié un nouveau phosphate de composition inconnue. La détermination de la structure cristalline de ce composé a montré qu'il s'agissait d'un nouveau type de pyrophosphate correspondante à la formule $LiInP_2O_7$. Nous décrivons dans ce qui suit la structure cristalline de ce nouveau composé.

Partie expérimentale. L'examen des clichés de précession a confirmé la symétrie monoclinique et les valeurs de paramètres de maille indiquées plus haut; cristal de dimensions d'environ 0,09 × 0,12 × 0,10 mm, diffractomètre CAD-4, monochromateur en lame graphite, exploration de la demi-sphère de réflexion pour $0 \leq \theta \leq 30°$ ($-9 \leq h \leq 9$, $-11 \leq k \leq 11$, $0 \leq l \leq 5$), mesure de 2712 réflexions; réflexions de contrôle: 025, 214 et 743; variation ≤1,4%; paramètres cristallins affinés à partir des angles θ ($12 < \theta < 30°$) de 25 réflexions déterminées par le diffractomètre, balayage ω, vitesse 0,02° s^{-1}, $\Delta\omega = 0{,}7° + 0{,}23\mathrm{tg}\theta$. Correction du facteur de Lorentz–polarisation, réflexions moyennées; 692 réflexions indépendantes avec $|F| > 2\sigma(F)$ conservées pour la détermination de la structure.

Détermination de la structure utilisant la méthode directe par l'application du programme *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) et par la synthèse de Fourier différence pour localiser l'atome de Li. Leurs coordonnées atomiques ont été affinées jusqu'aux valeurs correspondant aux indices résiduels: $R = 2{,}03\%$ et $wR = 2{,}59\%$; une autre série d'affinement utilisant les coordonnées énantiomorphes a conduit à un facteur wR plus élevé (2,9%), le présent model est donc adopté; $w = F_o/3F_{\max}$ si $F_o < F_{\max}$, $w = F_{\max}/3F_o$ si $F_o > F_{\max}$. Facteurs de diffusion dans *International Tables for X-ray Crystallography* (1974). Pas de corrections d'absorption ni d'extinction. Calculs effectués à l'aide du système de programme du *NRC* (Larson, Lee, Le Page & Gabe, 1982) sur le VAX 780. Affinement sur F. $(\Delta/\sigma)_{\max} = 0{,}18$. $|\Delta\rho| < 0{,}23$ e Å^{-3}. $S = 1{,}22$. Le Tableau 1 donne les positions atomiques et les facteurs thermiques

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