Table 2 reports the main interatomic distances and bond angles in these two rings. The two Ca atoms have a sevenfold coordination involving six O atoms and one water molecule, with Ca—O distances ranging from 2·339 to 2·471 Å. Within a range of 3·5 Å the first K atom, K(1), has seven neighbours and the second, K(2), has six. Table 2 gives the main interatomic distances in the associated cation polyhedra.

The network of hydrogen bonds is also reported in Table 2.

$CaNa_2P_4O_{12}.5{\cdot}5H_2O$. Table 3 reports the final atomic coordinates. In this second salt one observes the same feature as in the first: two different configurations for the P_4O_{12} ring anions. More interesting is the fact that one of these two configurations (*m*) has, until now, never been observed for this kind of anion.

The first P_4O_{12} group built up by P(1) and P(2) has binary symmetry, the second built up by P(3) and P(4) has mirror symmetry (Fig. 2), the mirror plane containing the two bonding O atoms, O(*L*33) and O(*L*44), being perpendicular to the ring plane.

Table 4 reports the main interatomic distances and bond angles for these two ring anions. The two Ca atoms have an eightfold coordination involving four O atoms and four water molecules, while the two Na atoms have distorted octahedral coordinations.

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Aluminium Decavanadate 25-Hydrate

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Abstract. $Al_2V_{10}O_{28}.25H_2O$, $M_r = 1461{\cdot}46$, orthorhombic, *Cmma*, $a = 21{\cdot}618\ (2)$, $b = 18{\cdot}414\ (2)$, $c = 10{\cdot}533\ (1)$ Å, $V = 4193\ (1)$ Å^3, $Z = 4$, $D_m = 2{\cdot}35$, $D_x = 2{\cdot}32$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 2{\cdot}19$ mm^{-1}, $F(000) = 2920$, $T = 298\ (2)$ K, $R = 3{\cdot}31\%$, $wR = 3{\cdot}49\%$ for 1474 independent observed reflections [$I > 5\sigma(I)$]. The unit cell contains four $(V_{10}O_{28})^{6-}$ anions located on sites of point symmetry $2/m$, four $[Al(OH_2)_6]^{3+}$ cations on $2/m$ sites, four $[Al(OH_2)_6]^{3+}$ cations on 222 sites and 52 lattice water molecules, four of which show occupational disorder. The compound presents a packing characterized by successive layers parallel to (100); ionic forces and H bonds between the layers and within them stabilize the structure.

Introduction. This study was undertaken as part of a research programme on crystal chemistry and physicochemical properties of hydrated decavanadate salts (Rigotti, Lavat, Escobar & Baran, 1983; Rivero, Punte, Rigotti & Navaza, 1985, and references therein). The title compound had been previously described as a 22-hydrate on the basis of TGA/DTA measurements (Rigotti *et al.*, 1983).

Experimental. $Al_2V_{10}O_{28}.25H_2O$ was synthesized according to the method described by Rigotti *et al.* (1983). Bright orange hexagonal plates were grown and kindly supplied by Dr E. J. Baran and co-workers, Programa QUINOR, UNLP, Argentina. Density measured pycnometrically. Crystal used for data collection defined by the following planes: ±(100) (0·125), ±(010) (0·125), ±(001) (0·165) (numbers in parentheses are the distances in mm from the crystal faces to an arbitrary origin inside the crystal). Cell

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Table 1. *Fractional positional parameters and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	B_{eq}*(Å^2)
V(1)	0·1498	0·1667	0·2046 (1)	1·77 (2)
V(2)	0·25	0·1613	0	1·27 (2)
V(3)	0·1260	0·25	−0·0468 (1)	1·54 (3)
V(4)	0·2727	0·25	0·2542 (1)	1·59 (3)
O(1)	0·2063 (1)	0·25	0·0894 (3)	1·3 (1)
O(2)	0·3120 (1)	0·1836 (1)	0·1269 (2)	1·44 (8)
O(3)	0·2060 (1)	0·1071 (1)	0·0900 (2)	1·77 (8)
O(4)	0·1015 (1)	0·3232 (1)	0·0584 (3)	1·85 (8)
O(5)	0·2778 (1)	0·1770 (1)	−0·3034 (3)	1·86 (8)
O(6)	0·3247 (2)	0·25	0·3632 (4)	2·5 (1)
O(7)	0·1176 (2)	0·25	0·2716 (4)	2·1 (1)
O(8)	0·0734 (2)	0·25	−0·1537 (4)	2·7 (1)
O(9)	0·1145 (1)	0·1035 (2)	0·2776 (3)	2·9 (1)
Al(1)	0·25	0	0·5	1·68 (7)
Al(2)	0	0	0	1·67 (7)
O*W*(1)	0·1620 (2)	0	0·5000 (0)	3·0 (1)
O*W*(2)	0·25	0	0·3220 (4)	2·4 (1)
O*W*(3)	0·25	0·1001 (2)	0·5	2·6 (1)
O*W*(4)	0·0867 (2)	0	0	2·4 (1)
O*W*(5)	0	0·0189 (2)	−0·1746 (4)	2·8 (1)
O*W*(6)	0	0·0996 (2)	0·0309 (4)	2·3 (1)
O*W*(7)	0·1504 (1)	0·0528 (2)	0·8010 (3)	3·3 (1)
O*W*(8)	0	0·1446 (3)	0·7112 (5)	4·6 (2)
O*W*(9)	0	0·0537 (3)	0·3937 (5)	5·0 (2)
O*W*(10)	0·1012 (2)	0·3735 (3)	0·5592 (4)	7·1 (2)
O*W*(11)†	0	0·2804 (6)	0·383 (1)	6·6 (2)

* Defined according to Hamilton (1959).
† Site occupation factor: 0·26 (1).

dimensions by least-squares refinement of 25 reflections ($17 < 2\theta < 25°$) on an Enraf/Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Scan width ($1 + 0{\cdot}34\tan\theta$)°, aperture ($1{\cdot}4 + 0{\cdot}8\tan\theta$) mm, maximum scan time 60 s. 2166 measured reflections ($h = 25$, $k = 21$, $l = 12$) in the range $3 < 2\theta < 50°$. Three standard reflections, 3·9% intensity variation, 1474 observed reflections [$I > 5\sigma(I)$] [this criterion was used owing to underestimation of $\sigma(I)$ during data collection]. Systematic absences: hkl: $h+k = 2n+1$; $hk0$: $h = 2n+1$. Lp correction; absorption correction (*SHELX*76), max. and min. transmission factors: 0·53, 0·49 for 047 and 2,0,11) respectively. The positions of four independent V^{5+} ions were obtained from a Patterson map; remaining non-hydrogen atoms from subsequent electron density synthesis. A ΔF synthesis after an anisotropic full-matrix least-squares refinement on F's to $R = 5{\cdot}1\%$ showed a peak of about 3·5 e Å^{-3} near an mm site that was interpreted as an occupationally disordered water oxygen. Further refinement with the disordered water oxygen isotropic dropped R to 4·6%. H's located from ΔF synthesis were included in the model with fixed positions. H(82) was kept, after several attempts to lower the O*W*(8)—H(82) distance (see Table 3), because it was the highest peak in the difference map and its inclusion allows a better convergence according to the Hamilton (1965) test. An overall isotropic thermal parameter was refined for most H's, the isotropic thermal parameters for the other H's were refined riding on those of bonded oxygens. Final refinement, with eight data per independent parameter, yielded $R = 3{\cdot}31\%$, $wR = 3{\cdot}49\%$; weighting scheme: $2{\cdot}45/[\sigma^2(F) + 0{\cdot}0016F^2]$. Maximum ratio of LS shift to e.s.d.: 0·065; final difference map was essentially flat, max. and min. heights of 0·57 and −0·45 e Å^{-3} near to V^{5+}. The calculations were performed on PDP 11/34 and IBM 4361 computers with *SHELX*76 (Sheldrick, 1976); atomic scattering factors for Al^{3+}, V^{5+} and O^{1-} (used for O in the decavanadate), from Cromer & Mann (1968); those for water oxygens (O*W*) supplied internally by *SHELX*. Final atomic positions and equivalent isotropic thermal parameters are given in Table 1.*

Discussion. The decavanadate polyanion is a discrete unit of ten distorted VO_6 octahedra (Fig. 1). Interatomic distances and angles within the VO_6 polyhedra show that its geometry is quite similar to that found in all the previously reported molecular structures for decavanadate salts (Evans, 1966; Swallow, Ahmed & Barnes, 1966; Saf'yanov & Belov, 1976; Saf'yanov, Kuz'min & Belov, 1978*a,b*; Durif, Averbuch-Pouchot & Guitel, 1980; Debaerdemaeker, Arrieta & Amigo, 1982; Rivero, Rigotti, Punte & Navaza, 1984; Rivero *et al.*, 1985). The complex ion structure has intrinsic symmetry *mmm* (Swallow *et al.*, 1966).

In the title compound dihedral angles [89·8 (2), 90·0 (1), 90·0 (1)°] and χ^2 values [$\sum(\Delta/\sigma)^2$] [3·81, 0·0] for the best least-squares planes corresponding to the ideal symmetry planes – calculated with a modified version of the program by Ahmed & Pippy (1970) –

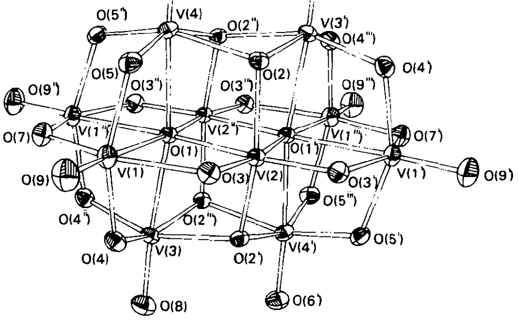

Fig. 1. Decavanadate polyanion with atom labels. Symmetry code: (i) $0{\cdot}5-x, y, -z$; (ii) $x, 0{\cdot}5-y, z$; (iii) $0{\cdot}5-x, 0{\cdot}5-y, z$. Ellipsoids enclose 40% probability.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond lengths and angles within the VO_6 polyhedra and best least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44384 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Coordination distances* (Å) *and the only angle* (°) *different from* 90° *in the* $[Al(OH_2)_6]^{3+}$ *polyhedra*; *e.s.d.'s in parentheses*

Al(1)–O*W*(1)	1·902 (4)	Al(2)–O*W*(4)	1·874 (4)
Al(1)–O*W*(2)	1·875 (4)	Al(2)–O*W*(5)	1·872 (4)
Al(1)–O*W*(3)	1·843 (4)	Al(2)–O*W*(6)	1·863 (4)

O*W*(5)–Al(2)–O*W*(6) 89·3 (2)

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°); *e.s.d.'s in parentheses*

D–H···*A*	*D*–H	*D*···*A*	H···*A*	*D*–H···*A*
O*W*(1)–H(1)···OW(10^{i})	0·89 (3)	2·746 (5)	1·88 (1)	168 (1)
O*W*(2)–H(2)···OW(7^{vi})	0·97 (3)	2·694 (4)	1·74 (2)	166 (1)
O*W*(3)–H(3)···O(5^{iii})	0·83 (2)	2·580 (6)	1·75 (3)	176 (1)
O*W*(4)–H(4)···OW(7^{v})	0·89 (3)	2·690 (5)	1·84 (3)	159 (1)
O*W*(5)–H(51)···OW(9^{x})	0·99 (1)	2·667 (2)	1·71 (2)	163 (1)
O*W*(5)–H(52)···OW(8^{v})	1·02 (1)	2·609 (4)	1·61 (4)	166 (1)
O*W*(6)–H(6)···O(4^{ii})	0·92 (2)	2·631 (4)	1·71 (2)	174 (1)
O*W*(7)–H(71)···O(2^{vi})	0·94 (4)	2·653 (4)	1·71 (2)	173 (1)
O*W*(7)–H(72)···OW(10^{ii})	0·99 (3)	3·076 (5)	2·16 (5)	153 (1)
O*W*(8)–H($81^{i,iv}$)···O($8^{vii,viii}$)	1·05 (3)	2·883 (5)	1·86 (4)	162 (2)
O*W*(8)–H($82^{i,iv}$)···OW($10^{ii,ix}$)	1·26 (3)	2·731 (5)	1·65 (5)	139 (2)
O*W*(10)–H(101)···O(6^{vi})	0·99 (3)	2·889 (5)	2·49 (5)	105 (2)
O*W*(11)–H($11^{i,iv}$)···O($7^{i,iv}$)	1·03 (5)	2·856 (6)	1·97 (4)	142 (2)

Symmetry codes: (i) x, y, z; (ii) $x, 0·5-y, z$; (iii) $0·5-x, y, -z$; (iv) $-x, y, z$; (v) $x, y, z-1$; (vi) $0·5-x, y, 1-z$; (vii) $-x, y, z+1$; (viii) $x, y, z+1$; (ix) $-x, 0·5-y, z$; (x) $-x, -y, -z$.

would indicate true *mmm* symmetry; however, differences of approximately four standard deviations were detected in the assumed mirror-symmetry-related pairs.* Therefore, the polyanions only present the crystallographic site symmetry (2/*m*). The diad axis [passing through V(2) and V(2^{ii})] is coincident with that found in pascoite (Swallow *et al.*, 1966). Departures from *mmm* symmetry are due to differences in V—O distances and V—O—V angles involving V_1, O*d* and O*g*-type atoms (Evans, 1966). O*d* and O*g*-type oxygens participate in strong hydrogen bonds connecting Al^{3+} polyhedra and polyanions, so those interactions might explain the observed distortions.

Al^{3+} ions occupy special positions and are octahedrally coordinated by six O*W* atoms. Bond lengths and angles within the polyhedra are given in Table 2, mean distances: Al(1)—O*W* = 1·87 (3), Al(2)—O*W* = 1·869 (5) Å. Similar values have been reported previously by Buchanan & Harris (1968), Fang & Robinson (1976) and Ginderow & Cesbron (1979) for Al^{3+} in an octahedral water environment.

Coordination octahedra around Al ions are distorted. Al(1)—O*W*(3) and Al(2)—O*W*(6) distances are shorter than the mean; these shortenings and the Al(1)—O*W*(1) lengthening may be understood on the grounds of the electrostatic valence rule (Pauling, 1960). Bond valence (bond strengths) *vs* bond length correlation (Baur, 1970; Brown & Shannon, 1973; Ferraris, Fuess & Joswig, 1986) shows that short donated H bonds correspond to large bond valences received by O*W* from the coordinated cation. From Tables 2 and 3 it can be seen that the above rule is fulfilled by O*W* coordinated to Al ions. These considerations do not agree completely with some experimental O*W*—H distances determined in this paper (Table 3), owing probably to the presence of heavy atoms (Baur, 1972).

The eleven non-equivalent lattice water molecules are involved in hydrogen bonds, as can be inferred from located H positions and donor–acceptor distances, Table 3. They are of different types according to their environment (Wells, 1975). Four [O*W*(1), O*W*(2), O*W*(4) and O*W*(5)] are coordinated by an Al ion and hydrogen bonded to two water molecules. Two [O*W*(3) and O*W*(6)] are coordinated by an Al ion and hydrogen bonded to two oxy-ion oxygens. One [O*W*(7)] links the two different kinds of cation polyhedra and is hydrogen bonded to three water molecules and one oxy-ion oxygen. The other four present some degree of disorder and their environments, which include water molecules and O atoms belonging to the polyanion, are not well defined.

The high thermal anisotropy exhibited by O*W*(8) ($U_{11} > U_{22} = U_{33}$)* might be explained by the presence of two mirror-plane-related O(8) and O*W*(10) atoms at hydrogen-bond distances, Table 3, which probably induce either static or dynamic orientational disorder.

O*W*(10) water molecules are situated on a layer centred at $z = 0·5$. This position reduces repulsion between polyanions related by a unit translation along **c**. Only one H atom, H(101), could be located and its site would suggest the presence of a bifurcated hydrogen bond (Chiari & Ferraris, 1982).

O*W*(9) water molecules build centrosymmetric dimers [O*W*(9)—O*W*(9) distance 2·988 (3) Å]; no H atoms belonging to this water could be located.

O*W*(11) water molecules are located near an *mm* site and present disorder across the mirror plane at $y = 0·25$ ($y = 0·75$). These waters fill an interionic space counterbalancing repulsive interactions between polyanions related by the mirror plane at $x = 0$ (and $x = 0·5$).

O*W*(9) dimers and O*W*(11) form a continuous chain along **b** [O*W*(9)—O*W*(11) contact: 3·057 (7) Å].

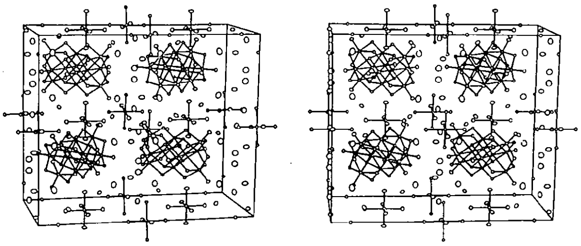

Fig. 2. Stereoscopic view of the unit cell down **c**, with **a** horizontal [both possible positions for O*W*(11) have been drawn].

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* See deposition footnote.

* See deposition footnote.

Fig. 2 shows a stereoscopic view of the unit cell. As can be seen, the packing in the [010] direction is characterized by successive layers of polyanions, centred at 0·25 and 0·75, and cation polyhedra, centred at 0 and 0·5. As analysis has shown, extensive hydrogen bonding within the layers and between them stabilizes the structure.

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Structure of 1,2;1,3;1,4-Tri-μ-carbonyl-1,2,2,2,3,3,3,4,4,4-decacarbonyl-2,3-μ-hydrido-*tetrahedro*-cobalttriruthenium

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Abstract. $[CoRu_3(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_{10}]$, $M_r = 727\cdot3$, monoclinic, $P2_1/n$, $a = 8\cdot486\ (1)$, $b = 15\cdot164\ (5)$, $c = 15\cdot688\ (1)$ Å, $\beta = 105\cdot92\ (1)°$, $V = 1941\cdot3\ (7)$ Å^3, $Z = 4$, $D_x = 2\cdot49$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 31\cdot5$ cm^{-1}, $F(000) = 1368$, $T = 298$ K, $R = 0\cdot0179$ for 2782 observed unique reflections. The directly observed hydrido ligand bridges an Ru—Ru edge [Ru—H 1·76 (4), 1·73 (4) Å]. The carbonyl ligand polytope with three bridging carbonyls bonded to cobalt is broadly similar to that found in the precursor anion $[CoRu_3(\mu\text{-}CO)_3(CO)_{10}]^-$, though the unusual skewed C_3 arrangement is not observed in the title complex.

Introduction. The isolobal relationship between the $AuPR_3$ unit and the H atom (Evans & Mingos, 1982; Lauher & Wald, 1981) has led to the suggestion that the easily determined position of the former moiety in transition-metal cluster compounds may allow prediction of the H-atom geometry in corresponding hydrido analogues (Lauher & Wald, 1981). This analogy becomes unreliable when more than one $AuPR_3$ unit is present owing to Au—Au bond formation (Braunstein & Rose, 1985; Hall & Mingos, 1984). From spectroscopic evidence it was proposed that the hydrido ligand in $[HCoRu_3(CO)_{13}]$ (1) bridged the Ru_3 face (Steinhardt, Gladfelter, Harley, Fox & Geoffroy, 1980), while a recent X-ray study on $[CoRu_3(\mu_3\text{-}AuPPh_3)(\mu\text{-}CO)_3(CO)_{10}]$ (Bruce & Nicholson, 1984) revealed the $AuPPh_3$ unit capping a $CoRu_2$ face. Our interest in the use of monohydrido cluster complexes as precursors for the synthesis of Hg-bridged compounds (Farrugia, 1987) prompted an examination of the structure of (1).

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