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Phosphonoacetic Acid (H_3AP) and its Salts $KH_2AP.H_2O$, $(NH_4)H_2AP$, LiH_2AP, $NaH_2AP.2H_2O$, K_2HAP, $(NH_4)_2HAP$, $Na_2HAP.2H_2O$, $(NH_4)_3AP.2H_2O$ and $Na_3AP.10H_2O$

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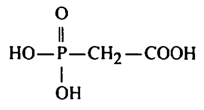
Abstract

The crystal structures of phosphonoacetic acid, $C_2H_5O_5P$ [H_3AP, (I)], and its salts potassium phosphonoacetate hydrate, $K^+.C_2H_4O_5P^-.H_2O$ [$KH_2AP.H_2O$, two crystalline forms, α, (II), and β, (III)], ammonium phosphonoacetate, $NH_4^+.C_2H_4O_5P^-$ [$(NH_4)H_2AP$, (IV)], lithium phosphonoacetate, $Li^+.C_2H_4O_5P^-$ [LiH_2AP, (V)], sodium phosphonoacetate dihydrate, $Na^+.C_2H_4O_5P^-.2H_2O$ [$NaH_2AP.2H_2O$, (VI)], dipotassium phosphonoacetate, $2K^+.C_2H_3O_5P^{2-}$ [K_2HAP, (VII)], diammonium phosphonoacetate, $2NH_4^+.C_2H_3O_5P^{2-}$ [$(NH_4)_2HAP$, (VIII)], disodium phosphonoacetate dihydrate, $2Na^+.C_2H_3O_5P^{2-}.2H_2O$ [$Na_2HAP.2H_2O$, (IX)], triammonium phosphonoacetate dihydrate, $3NH_4^+.C_2H_2O_5P^{3-}.2H_2O$ [$(NH_4)_3AP.2H_2O$, (X)], and trisodium phosphonoacetate decahydrate, $3Na^+ . C_2H_2O_5P^{3-} . 10H_2O$ [$Na_3AP.10H_2O$, (XI)], are described. In all cases, one of the phosphonate O atoms (denoted O2) is nearly antiperiplanar to the carboxylic C1 atom. There is also an evident tendency for the plane through the carboxyl group to be almost perpendicular to the plane through the methylene C atom C2, P and O2. In the acid anions, the dihedral angles between these planes range from 75.6 (1)° in compound (V) to 89.0 (1)° in compound (VII), whereas in the free acid, (I), this angle is 50.6 (1)°.

Comment

Phosphonoacetic acid (H_3AP) is one of the simplest phosphonocarboxylic acids, all of which formally may exist in four different forms: tribasic acid, monoanion, dianion and trianion. All these forms are represented in the structures described here. Until now, the only structurally characterized phosphonoacetic acid derivative was 2-amino-5-nitropyridinium phosphonoacetate (Pécaut & Masse, 1994). We now continue our investigations on phosphonate analogs of phosphate esters (Weichsel & Lis, 1996) by presenting the structures of compounds (I)–(XI). The same atom-numbering scheme has been used for each AP residue in these structures.

The structure of phosphonoacetic acid, (I), is shown in Fig. 1. Of the two phosphonic hydroxyl O atoms, O2 is *trans* and the O1 is *gauche* with respect to the carboxylic atom C1. The unprotonated O3 atom is also *gauche* with respect to C1. The dihedral angle between the carboxyl group and plane through O2—P—C2 is 50.6 (1)°. The crystal packing and hydrogen-bonding schemes are shown in Fig. 2. The unprotonated O3 atom of the phosphonic group accepts two H atoms, whereas the hydroxyl groups act as donors only, forming a network. All hydrogen bonding may be classified as medium strong [Table 2(*b*)].



$$HO{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}CH_2{-}COOH$$

(I)

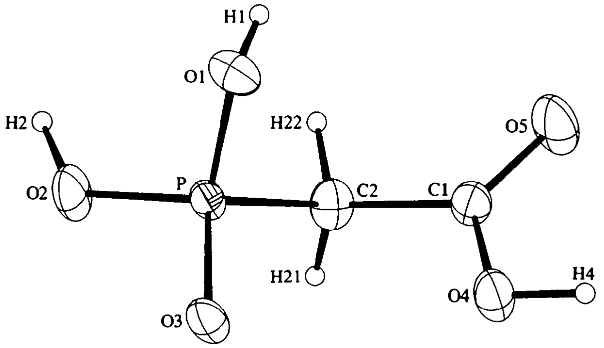


Fig. 1. The structure and numbering scheme of the molecule of phosphonoacetic acid, (I). Displacement ellipsoids are shown at the 50% probability level.

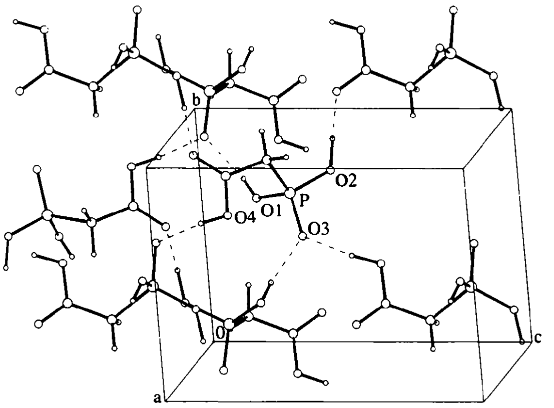
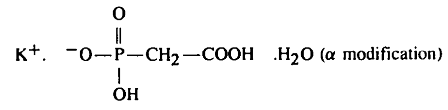


Fig. 2. The packing in the phosphonoacetic acid crystal, (I). Dashed lines show hydrogen bonds.

The crystals of potassium phosphonoacetate hydrate (α modification), (II), are composed of K^+ cations, phosphonoacetate monoanions (Fig. 3) and water of hydration. The overall structure of the anion is similar to the acid molecule of (I). The deprotonated O2 atom is *trans* to C1. The K^+ cation is octacoordinate, participating in K···O distances of 2.665 (2)–3.155 (2) Å. Each K^+ ion is coordinated to five independent anions and one water molecule. The carboxylic O4 atom (as donor) forms a hydrogen bond with the phosphonate O3 atom. The O6 water molecule forms two donor hydrogen bonds and one acceptor hydrogen bond with three phosphonate O atoms of three adjacent anions [Fig. 4 and Table 4(*b*)].



$$\mathrm{K^{+}.\ \ {}^{-}O{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}CH_2{-}COOH\ \ .H_2O}\ \text{(α modification)}$$

(II)

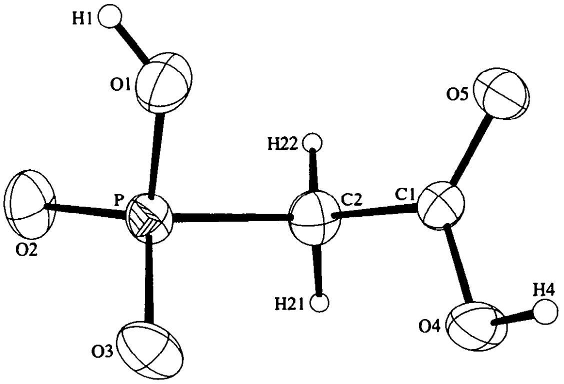


Fig. 3. The molecular structure of the phosphonoacetate monoanion in (II). Displacement ellipsoids are shown at the 50% probability level.

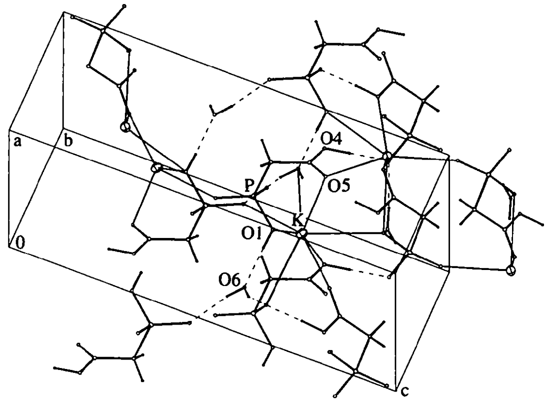
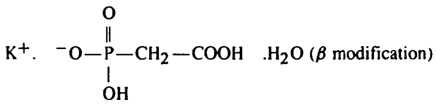


Fig. 4. The packing in the crystal of (II).

The crystals of potassium phosphonoacetate hydrate (*β* modification), (III), have the same formula as those of compound (II) and crystallize in the same space group. Furthermore, the conformation of the anion (Fig. 5) is very similar to that found in (II). The differences are manifested in the P—O bond lengths. These differences may be a consequence of the different potassium coordination and hydrogen-bonding scheme [Fig. 6 and Table 6(*b*)]. The K^+ cation is octacoordinate, participating in K···O distances of 2.813 (2)–3.100 (2) Å. The ninth O atom is at 3.419 (2) Å. Each K^+ ion is coordinated to five independent anions and two water molecules. The carboxylic O4 atom (as donor) forms a hydrogen bond with the phosphonate O3^{ii} atom [symmetry code as in Table 6(*b*)]. The water O6 molecule forms (as donor) two hydrogen bonds with two adjacent anions and bridges two symmetry-related K^+ cations.



$$\mathrm{K^{+}.\ \ {}^{-}O{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}CH_2{-}COOH\ \ .H_2O}\ \text{(β modification)}$$

(III)

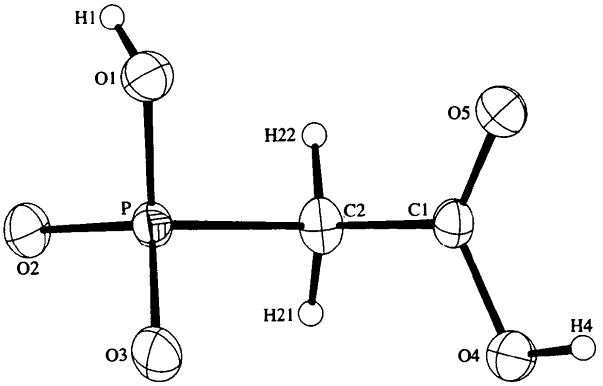


Fig. 5. The molecular structure of the phosphonoacetate monoanion in (III). Displacement ellipsoids are shown at the 50% probability level.

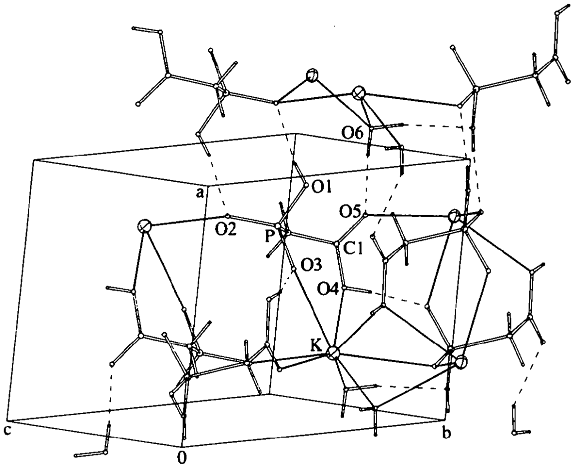
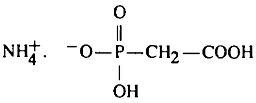


Fig. 6. The packing in the crystal of (III).

The crystals of ammonium phosphonoacetate, (IV), are built up from phosphonoacetate monoanions and ammonium cations. The overall structure of the monoanion is similar to those found in both potassium modifications. All N- and O-bonded H atoms are utilized in intermolecular hydrogen bonding [Table 8(*b*) and Fig. 7]. The H14 atom is utilized in a weak bifurcated hydrogen bond bridging two O5 atoms from adjacent anions. The NH_4^+ cations thus bridge through carboxylic and phosphonate O atoms to five symmetry-related monoanions. A three-dimensional network of hydrogen bonds is completed by links between phosphonic groups and by carboxylic-to-phosphonate interactions.



$$NH_4^+ \cdot \; ^-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-CH_2-COOH$$

(IV)

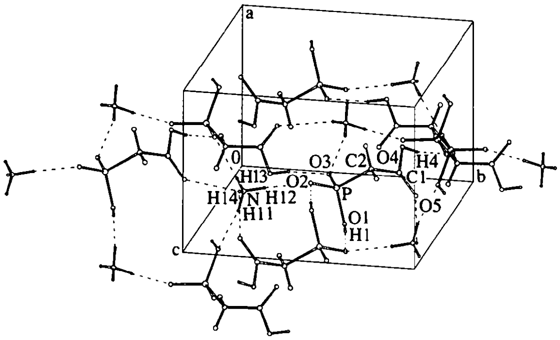
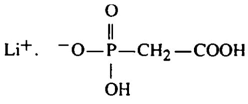


Fig. 7. The packing in the crystal of (IV).

The crystals of lithium phosphonoacetate, (V), are composed of Li^+ cations and phosphonoacetate monoanions (Fig. 8). In contrast to compounds (II)–(IV), the phosphonate hydroxyl group is in a *syn* orientation with respect to the carboxylic OH group, whereas in 2-amino-5-nitropyridinium phosphonoacetate, the phosphonate hydroxyl group is in a *trans* position with respect to the carboxylic C atom (Pécaut & Masse, 1994). The Li coordination number is four and the Li^+ cation bonds to four O atoms of four phosphonoacetate anions. The coordination polyhedron is a distorted tetrahedron. The $Li^+\cdots O$ distances [1.923 (3)–2.012 (3) Å] are in agreement with other salts of tetracoordinated Li^+ (Popek & Lis, 1996). The packing and hydrogen-bonding scheme are illustrated in Fig. 9. The carboxylic and phosphonic OH groups form (as donor) medium strong hydrogen bonds [Table 10(*b*)] with unprotonated phosphonate O atoms of adjacent anions, forming cyclic centrosymmetric dimers.



$$Li^+ \cdot \; ^-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-CH_2-COOH$$

(V)

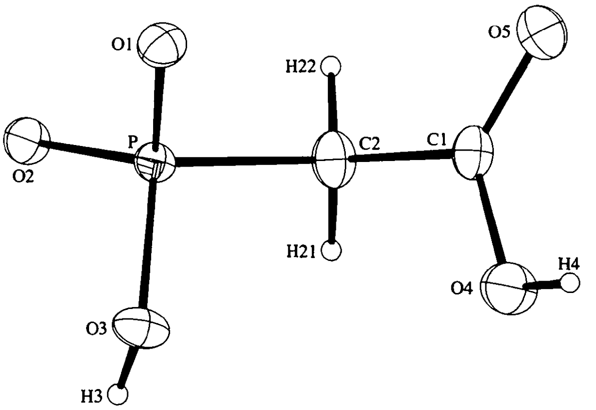


Fig. 8. The molecular structure of the phosphonoacetate monoanion in (V). Displacement ellipsoids are shown at the 50% probability level.

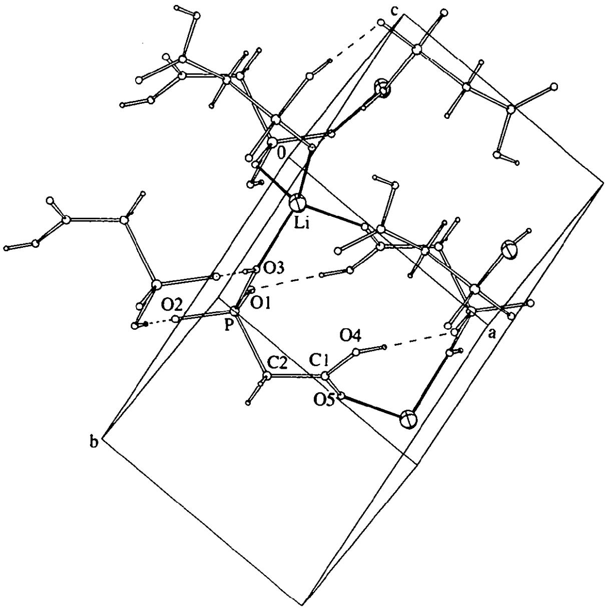
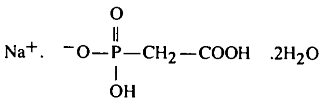


Fig. 9. The packing in the crystal of (V).

The asymmetric unit of sodium phosphonoacetate dihydrate, (VI), contains two phosphonoacetate monoanions (denoted *A* and *B*), two Na^+ cations and four water molecules. The structures of the two crystallographically independent anions are similar to those found in compounds (II)–(IV). Both crystallographically independent Na^+ cations have distorted octahedral coordination, with $Na\cdots O$ distances of 2.329 (3)–2.558 (2) Å. The packing and hydrogen-bonding scheme are shown in Fig. 10. All hydroxyl groups are involved in hydrogen bonding. The phosphonate and carboxylic OH groups form (as donors) strong hydrogen bonds with unprotonated phosphate O atoms. All other hydrogen bonds are relatively weak [Table 12(*b*)].



$$Na^+ \cdot \; ^-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-CH_2-COOH \;.2H_2O$$

(VI)

The crystals of dipotassium phosphonoacetate, (VII), are composed of phosphonoacetate dianions (Fig. 11) and two crystallographically independent K^+ cations.

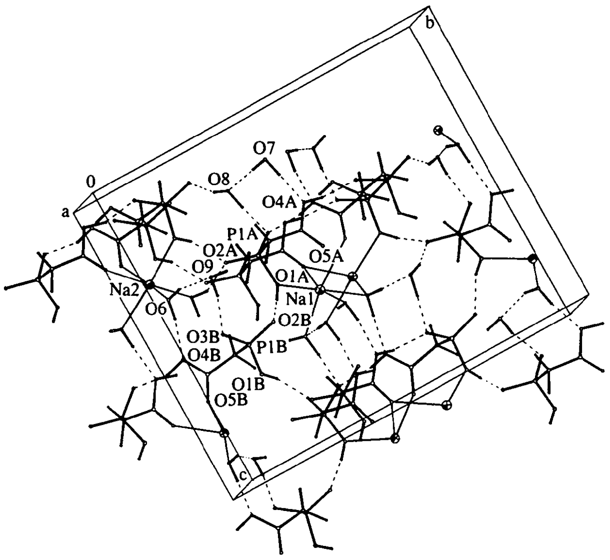


Fig. 10. The packing in the crystal of (VI).

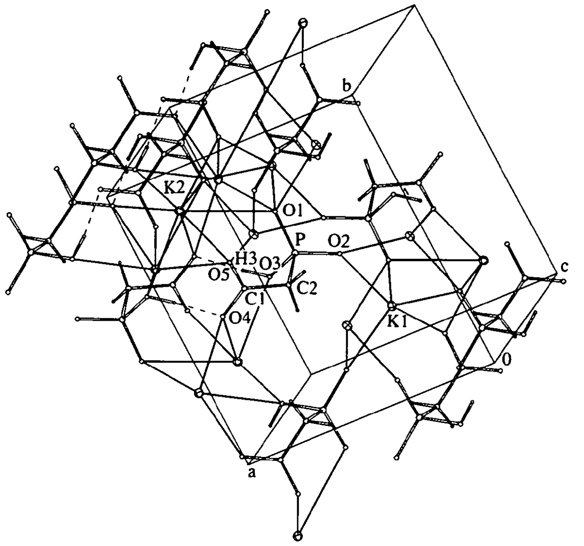
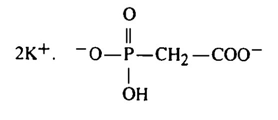
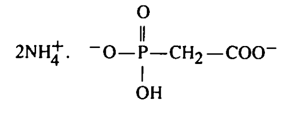


Fig. 12. The packing in the crystal of (VII).



$$2K^+ \cdot \; {}^-O-\underset{\underset{\textstyle OH}{|}}{\overset{\overset{\textstyle O}{\|}}{P}}-CH_2-COO^-$$

(VII)



$$2NH_4^+ \cdot \; {}^-O-\underset{\underset{\textstyle OH}{|}}{\overset{\overset{\textstyle O}{\|}}{P}}-CH_2-COO^-$$

(VIII)

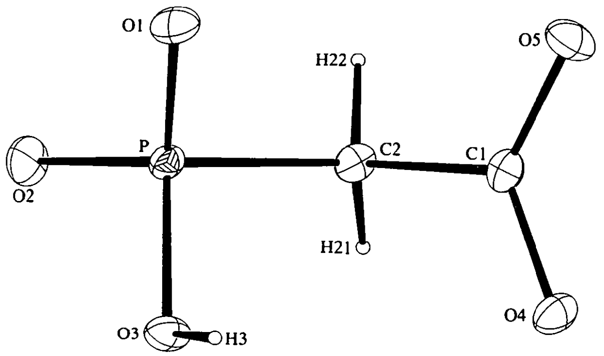


Fig. 11. The molecular structure of the phosphonoacetate olianion in (VII). Displacement ellipsoids are shown at the 50% probability level.

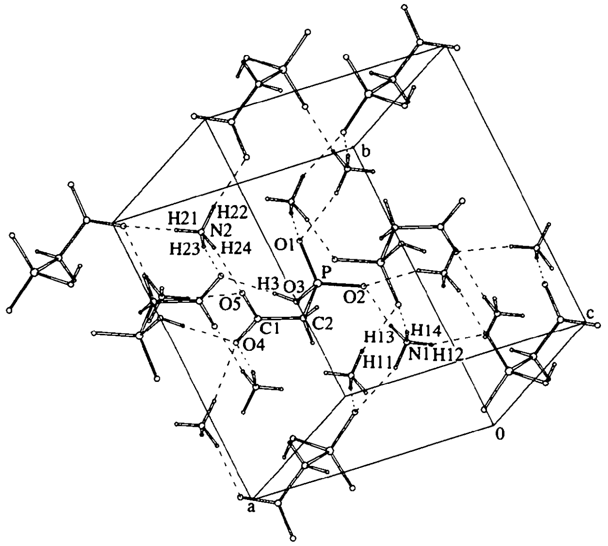
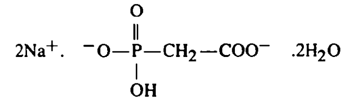


Fig. 13. The packing in the crystal of (VIII).

The deprotonated carboxylate group is perpendicular to the plane through the C2, P and O2 atoms. The hydroxyl O3—H3 group is utilized in hydrogen bonding with the O4 atom from an adjacent anion, forming a cyclic centrosymmetric system of hydrogen bonds [Table 14(*b*) and Fig. 12]. The K^+ cations coordinate to O atoms, forming rather distorted polyhedra. K1 is coordinated to five O atoms at distances of 2.660 (2)–2.814 (2) Å; other K1···O distances are longer than 3.4 Å. The K2 cation has seven neighbors at 2.710 (2)–2.965 (2) Å; the next, eighth neighbor, is at a distance of 3.275 (2) Å.

The crystals of the diammonium salt diammonium phosphonoacetate, (VIII), are isomorphous with those of the dipotassium salt, (VII). The hydroxyl O3—H3 group is utilized in hydrogen bonding with the O4 atom of an adjacent anion as in (VII). The ammonium cations are utilized in hydrogen bonds, forming a three-dimensional hydrogen-bonding network [Fig. 13 and Table 16(*b*)].

The asymmetric unit of disodium phosphonoacetate dihydrate, (IX), contains two Na^+ cations, a phosphonoacetate dianion and two water molecules. One of the water molecules is disordered in such a way that two O7 and O71 atoms (both with occupancy factors of 0.5) are 0.72 (1) Å apart, but the H7 and H71 atoms occupy nearly identical positions and form similar hydrogen bonds. The hydroxyl O3—H3 group of one anion is utilized (as a donor) in hydrogen bonding with the O4 atom of an adjacent anion, forming a cyclic centrosymmetric system of hydrogen bonds [Table 18(*b*) and Fig. 14]. The O2 atom accepts three hydrogen bonds from water molecules. The Na2 atom coordinates to the O6 water molecule and to four O atoms from four symmetry-related anions at 2.316 (2)–2.438 (2) Å. The sixth corner of a distorted octahedron [at 2.900 (5) Å] is occupied by the O4 atom at $x - \frac{1}{2}, \frac{1}{2} + y, z$. The distorted octahedron around Na1 is formed by five phosphonoacetate O atoms and the sixth corner by disordered O7 or O71 water molecules.



$$2\mathrm{Na}^+ .\ {}^-\mathrm{O}-\overset{\overset{\displaystyle\mathrm{O}}{\|}}{\underset{\underset{\displaystyle\mathrm{OH}}{|}}{\mathrm{P}}}-\mathrm{CH_2}-\mathrm{COO}^-\ \ .2\mathrm{H_2O}$$

(IX)

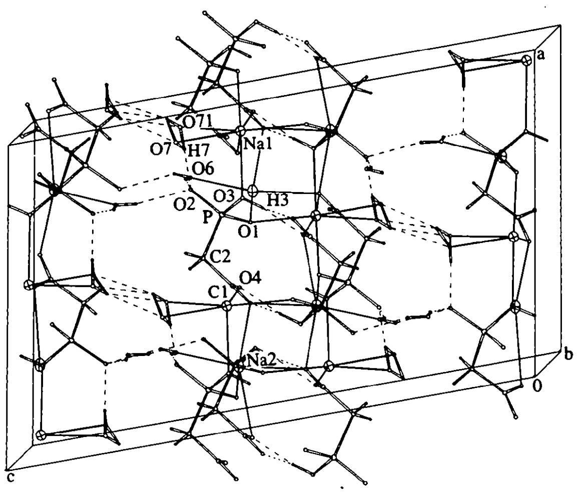
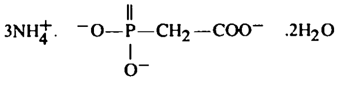


Fig. 14. The packing in the crystal of (IX). Both disordered O7 and O71 water molecules (with occupancy factor 0.5) are shown.

The crystals of triammonium phosphonoacetate dihydrate, (X), are built up of phosphonoacetate trianions (Fig. 15), three crystallographically independent NH_4^+ cations and two water molecules. Dimensions of the hydrogen-bonding structure shown in Fig. 16 are given in Table 20(*b*). The phosphonate O1 and carboxylate O4 and O5 atoms accept two hydrogen bonds, and the remaining phosphonate O2 and O3 atoms each accept three hydrogen bonds. Both water molecules are involved in four hydrogen bonds (two as donors and two as acceptors).



$$3\mathrm{NH_4^+} .\ {}^-\mathrm{O}-\overset{\overset{\displaystyle\mathrm{O}}{\|}}{\underset{\underset{\displaystyle\mathrm{O}^-}{|}}{\mathrm{P}}}-\mathrm{CH_2}-\mathrm{COO}^-\ \ .2\mathrm{H_2O}$$

(X)

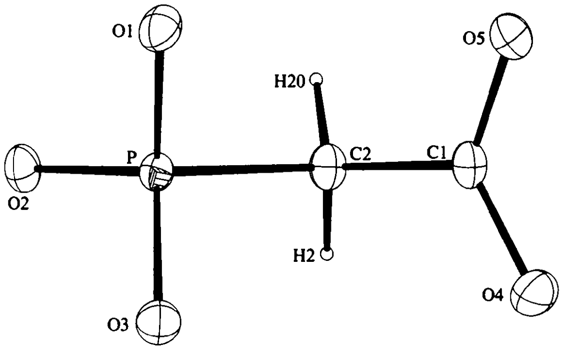


Fig. 15. The molecular structure of the phosphonoacetate trianion in (X). Displacement ellipsoids are shown at the 50% probability level.

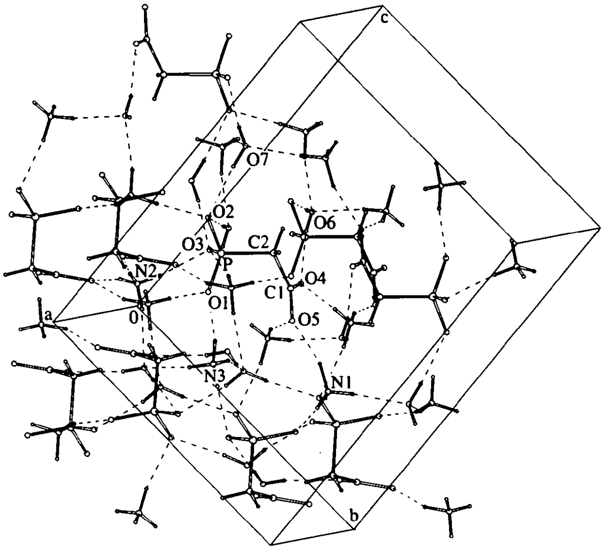
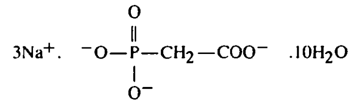


Fig. 16. The packing in the crystal of (X).

The crystals of trisodium phosphonoacetate decahydrate, (XI), are composed of phosphonoacetate trianions, five crystallographically independent Na^+ cations and 13 crystallographically independent water molecules. The Na5 atom and O18 water molecule are cooperatively disordered around a mirror plane in such a way that, when Na5 is at one side of the mirror plane then O18 is on the opposite side, and *vice versa*; the Na5···O18 distance is then 2.412 (4) Å. The packing arrangement is shown in Fig. 17. All phosphonoacetate O atoms are utilized in hydrogen bonding [Table 22(*b*)]. The O2 atom accepts four H atoms and is thus formally pentacoordinate. This situation is sometimes observed in organic phosphate crystals (Lis, 1993). The O4 atom accepts three H atoms and coordinates to Na3. The O5 atom accepts two H atoms and coordinates to a disordered Na5 atom or accepts atom H18 of the disordered O18 water molecule. Three Na^+ cations (Na1, which occupies general position, Na2, which lies on center of symmetry and Na4, which is on a mirror plane) are coordinated only to water molecules forming distorted octahedra. The disordered Na5 atom is pentacoordinate (three waters, carboxylate O5 atom and disordered O18 water molecule). Na3 is hexacoordinate (four water molecules and two symmetry-related O4 atoms). The disordered O18 water molecules occupy the sixth corners. All water molecules are engaged in the formation of hydrogen bonds [Table 22(*b*)].



$$3Na^{+} .\ {}^{-}O-\underset{O^{-}}{\underset{|}{\overset{O}{\overset{\|}{P}}}}-CH_2-COO^{-}\ .10H_2O$$

(XI)

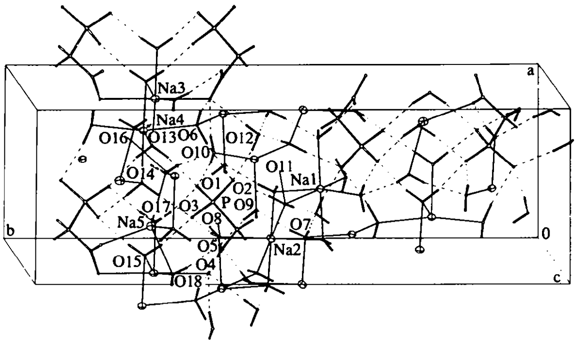


Fig. 17. The packing in the crystal of (XI).

In this work, the molecular structures of phosphonoacetates at all levels of protonation have been described. The crystallization of the AP residue in different ionization states from water solutions suggests that it is stable over a large range of pH. On going from phosphonoacetic acid to the tri-ionized anion, it is apparent that the first proton to dissociate comes from the phosphonic group, that the second H atom to dissociate is lost from the carboxylic group and that the third dissociation involves the second (less acidic) H atom from the phosphonic group.

The main points of interest in the AP structures are the phosphonate-group orientation with respect to the carboxyl group, the deviation of the phosphonate group from a tetrahedral shape and the P—O and P—C bond lengths.

The orientation of the phosphonate group with respect to the acetate group may be described (Table 23) by ϕ, the dihedral angle between the carboxyl group and the plane through O2, P and C2 or by the O2—P—C2—C1 and P—C2—C1—O torsion angles.

The similar overall structure of the AP residues (in different chemical environments and different ionization stages) suggests that the conformation of the AP residue as a whole is very stable. In all cases, one of the phosphonate O atoms (denoted O2) is nearly *trans* with respect to the carboxyl C1 atom. There is also an evident tendency for the plane through the carboxyl group to be almost perpendicular to the plane through the C2, P and O2 atoms. The dihedral angles, ϕ, range from 75.6 (1)° in compound (V) to 89.0 (1)° in compound (VII), falling to 50.6 (1)° in (I). The fully ionized phosphonate groups in compounds (X) and (XI) have nearly ideal C_{3v} symmetry; the P—O distances and O—P—O and O—P—C bond angles do not differ significantly, and the O—P—O bond angles (average 111.8°) are larger than the O—P—C bond angles (average 107.0°). More deformation from tetrahedral shape is observed in mono-ionized phosphonate groups, where the largest O—P—O bond angle involves unprotonated O atoms. The P—O(H) bond distances, which range from 1.551 (2) Å in compound (III) to 1.597 (2) Å in compound (IX), are longer than the P—O bonds. In the acid crystal, (I), the two P—O(H) bond lengths have similar values and the largest bond angle is between the unprotonated O atom and C2. The shortest P—C2 bond distance is in (I) [1.799 (2) Å]. In the other crystals, this bond length ranges from 1.804 (2) to 1.824 (2) Å.

The bond lengths and angles in the acetic or acetate groups are unexceptional. Like other compounds with the same groups (Sawka-Dobrowolska, Głowiak & Barycki, 1989; Sawka-Dobrowolska & Barycki, 1989), the phosphonic and carboxylic groups are linked by hydrogen bonds.

Experimental

Commercially available (Aldrich) phosphonoacetic acid was recrystallized from water solution. Except for $(NH_4)_3AP.2H_2O$, (X), all other crystalline compounds were obtained by slow concentration of aqueous solutions of phosphonoacetic acid and Li_2CO_3, NH_4HCO_3, KOH or NaOH in approximate stoichiometric ratios. The $(NH_4)_3AP.2H_2O$ crystals were obtained when a saturated aqueous solution of $(NH_4)_2HAP$, (VIII), was allowed to stand over solid NH_4HCO_3 in a desiccator. The crystal of (I) was held in a capillary tube. The crystals measured at room temperature were coated with lacquer. $KH_2AP.H_2O$ was first isolated as large columns [crystal (II); α modification]. After recrystallization, the second form [crystal (III); β modification] was obtained. Crystals of K_2HAP, (VII), are hygroscopic and unstable in air. For $NaH_2AP.2H_2O$, (VI), preliminary examinations were by oscillation and Weissenberg photographs. Density, D_m, was measured by flotation in CCl_4/1,2-dibromoethane at room temperature for all compounds except (III) and (X) where crystal density was not measured.

Compound (I)

Crystal data

$C_2H_5O_5P$
$M_r = 140.03$
Orthorhombic
$P2_12_12_1$
$a = 6.090\,(4)$ Å
$b = 7.660\,(4)$ Å
$c = 10.356\,(7)$ Å
$V = 483.1\,(5)$ Å^3
$Z = 4$
$D_x = 1.925\,(3)$ Mg m^{-3}
$D_m = 1.91$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 10$–$16°$
$\mu = 0.496$ mm^{-1}
$T = 298\,(1)$ K
Thick plate
0.6 × 0.5 × 0.3 mm
Colorless

Data collection

Kuma KM-4 automatic diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2760 measured reflections
2115 independent reflections
1913 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0164$
$\theta_{\rm max} = 35°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 16$
3 standard reflections monitored every 50 reflections intensity decay: −12%

Refinement

Refinement on F^2
$R(F) = 0.0252$
$wR(F^2) = 0.0680$
$S = 1.135$
2115 reflections
94 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.024P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.12$
$\Delta\rho_{\rm max} = 0.41$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.29$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.042 (6)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = 0.43 (8)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
P	0.37923 (4)	0.73391 (3)	0.34282 (2)	0.01603 (7)
O1	0.5993 (2)	0.76878 (13)	0.27349 (9)	0.0252 (2)
O2	0.3667 (2)	0.82885 (12)	0.47410 (8)	0.0276 (2)
O3	0.3566 (2)	0.54270 (10)	0.36793 (8)	0.0228 (2)
O4	0.1625 (2)	0.58018 (11)	0.10264 (8)	0.0279 (2)
O5	0.1606 (3)	0.84005 (13)	0.01025 (9)	0.0347 (3)
C1	0.1625 (2)	0.75046 (14)	0.10712 (10)	0.0194 (2)
C2	0.1650 (2)	0.82175 (15)	0.24237 (11)	0.0215 (2)

Table 2. *Selected geometric parameters (Å, °) for (I)*

(*a*) Bonds lengths, angles and torsions

P—O1	1.544 (2)	C1—C2	1.503 (2)
P—O2	1.544 (2)	O4—C1	1.305 (2)
P—O3	1.494 (2)	O5—C1	1.216 (2)
P—C2	1.799 (2)		
O1—P—O2	111.8 (1)	O3—P—C2	113.6 (1)
O1—P—O3	109.3 (1)	C1—C2—P	114.2 (1)
O2—P—O3	107.7 (1)	O4—C1—C2	113.3 (1)
O1—P—C2	107.2 (1)	O5—C1—C2	124.3 (2)
O2—P—C2	107.3 (1)	O5—C1—O4	122.3 (2)
O1—P—C2—C1	56.3 (2)	O4—C1—C2—P	52.0 (2)
O2—P—C2—C1	176.5 (2)	O5—C1—C2—P	−128.0 (2)
O3—P—C2—C1	−64.5 (2)		

(*b*) Hydrogen-bonding geometry

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O3$^{\rm i}$	0.75 (3)	1.83 (3)	2.573 (2)	171 (3)
O2—H2···O5$^{\rm ii}$	1.05 (4)	1.52 (4)	2.569 (2)	172 (4)
O4—H4···O3$^{\rm iii}$	0.95 (3)	1.66 (3)	2.609 (2)	174 (3)

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, 2 - y, \frac{1}{2} + z$; (iii) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$.

Compound (II)

Crystal data

$K^+.C_2H_4O_5P^-.H_2O$
$M_r = 196.14$
Monoclinic
$P2_1/c$
$a = 6.990$ (4) Å
$b = 6.266$ (3) Å
$c = 15.932$ (8) Å
$\beta = 98.41$ (4)°
$V = 690.3$ (6) Å^3
$Z = 4$
$D_x = 1.887$ (3) Mg m^{-3}
$D_m = 1.90$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 28 reflections
$\theta = 10$–21°
$\mu = 0.974$ mm^{-1}
$T = 297$ (1) K
Large column
0.45 × 0.40 × 0.25 mm
Colorless

Data collection

Kuma KM-4 automatic diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3102 measured reflections
3042 independent reflections
2418 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0275$
$\theta_{\rm max} = 35°$
$h = -11 \rightarrow 1$
$k = 0 \rightarrow 10$
$l = -24 \rightarrow 25$
3 standard reflections monitored every 100 reflections intensity decay: 3%

Refinement

Refinement on F^2
$R(F) = 0.0353$
$wR(F^2) = 0.0923$
$S = 1.124$
3042 reflections
116 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 0.068P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.148$

$\Delta\rho_{\rm max} = 0.62$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.42$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.019 (3)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
K	0.32783 (4)	0.60256 (6)	0.67421 (2)	0.03199 (9)
P	0.78817 (4)	0.35774 (5)	0.58276 (2)	0.02185 (8)
O1	0.6323 (2)	0.2951 (2)	0.64106 (7)	0.0331 (2)
O2	0.7305 (2)	0.2891 (2)	0.49286 (6)	0.0335 (2)
O3	0.9841 (2)	0.2854 (2)	0.62620 (6)	0.0330 (2)
O4	0.9882 (2)	0.7248 (2)	0.71526 (7)	0.0351 (2)
O5	0.6749 (2)	0.7869 (2)	0.71009 (7)	0.0364 (2)
O6	0.3195 (2)	0.0687 (2)	0.59975 (9)	0.0401 (3)
C1	0.8099 (2)	0.7285 (2)	0.67586 (7)	0.0234 (2)
C2	0.7872 (2)	0.6465 (2)	0.58638 (7)	0.0249 (2)

Table 4. *Selected geometric parameters (Å, °) for (II)*

(*a*) Bonds lengths, angles and torsions

K—O1	2.975 (2)	P—O1	1.581 (2)
K—O1$^{\rm i}$	3.155 (2)	P—O2	1.493 (2)

K—O2^{ii}	2.719 (2)	P—O3	1.511 (2)
K—O3^{iii}	3.126 (2)	P—C2	1.810 (2)
K—O4^{iii}	2.665 (2)	C1—C2	1.502 (2)
K—O5	2.672 (2)	O4—C1	1.312 (2)
K—O5^{iv}	2.706 (2)	O5—C1	1.213 (2)
K—O6^{v}	3.150 (2)		
O2—P—O1	112.3 (1)	O1—P—C2	102.9 (1)
O3—P—O1	108.2 (1)	C1—C2—P	111.8 (1)
O2—P—O3	116.9 (1)	O4—C1—C2	114.1 (2)
O2—P—C2	108.5 (1)	O5—C1—C2	123.3 (2)
O3—P—C2	107.0 (1)	O5—C1—O4	122.5 (2)
O1—P—C2—C1	51.0 (2)	O3—P—C2—C1	−63.0 (2)
O2—P—C2—C1	170.1 (1)	O4—C1—C2—P	79.0 (2)

Symmetry codes: (i) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (ii) $1-x, 1-y, 1-z$; (iii) $x-1, y, z$; (iv) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; (v) $x, 1+y, z$.

(*b*) Hydrogen-bonding geometry

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O6	0.81 (3)	1.80 (3)	2.609 (2)	177 (3)
O4—H4···O3^{i}	0.98 (3)	1.55 (3)	2.533 (2)	178 (3)
O6—H61···O2^{ii}	0.77 (3)	1.92 (3)	2.679 (2)	167 (3)
O6—H62···O3^{iii}	0.94 (4)	1.88 (4)	2.795 (2)	164 (4)

Symmetry codes: (i) $2-x, \frac{1}{2}+y, \frac{3}{2}-z$; (ii) $1-x, -y, 1-z$; (iii) $x-1, y, z$.

Compound (III)

Crystal data

$K^+.C_2H_4O_5P^-.H_2O$
$M_r = 196.14$
Monoclinic
$P2_1/c$
$a = 7.949\ (4)$ Å
$b = 9.931\ (5)$ Å
$c = 8.407\ (4)$ Å
$\beta = 99.73\ (4)°$
$V = 654.1\ (6)$ Å^3
$Z = 4$
$D_x = 1.992\ (2)$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 10–17°$
$\mu = 1.028$ mm^{-1}
$T = 297\ (2)$ K
Thick plate
0.3 × 0.3 × 0.1 mm
Colorless

Data collection

Kuma KM-4 automatic diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3523 measured reflections
2838 independent reflections
1966 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0265$
$\theta_{\rm max} = 35°$
$h = -12 \rightarrow 5$
$k = 0 \rightarrow 16$
$l = -13 \rightarrow 13$
3 standard reflections monitored every 50 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.0375$
$wR(F^2) = 0.0934$
$S = 1.084$
2466 reflections
120 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.059P)^2 + 0.066P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.084$
$\Delta\rho_{\rm max} = 0.72$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.36$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (III)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
K†	0.2713 (2)	0.67309 (5)	0.18694 (7)	0.0291 (2)
K1‡	0.211 (7)	0.678 (3)	0.175 (4)	0.029 (6)
P	0.74585 (5)	0.56082 (4)	0.40482 (5)	0.0174 (1)
O1	0.9066 (2)	0.60780 (13)	0.3382 (2)	0.0238 (3)
O2	0.7863 (2)	0.43454 (12)	0.5077 (2)	0.0250 (3)
O3	0.5969 (2)	0.54572 (13)	0.2703 (2)	0.0261 (3)
O4	0.4810 (2)	0.84142 (14)	0.4082 (2)	0.0255 (3)
O5	0.7515 (2)	0.90274 (14)	0.4161 (2)	0.0269 (3)
O6	1.0974 (2)	0.8599 (2)	0.3690 (2)	0.0345 (4)
C1	0.6470 (2)	0.8230 (2)	0.4489 (2)	0.0181 (3)
C2	0.6935 (3)	0.6930 (2)	0.5368 (2)	0.0206 (3)

† Site occupancy = 0.974 (7). ‡ Site occupancy = 0.026 (7).

Table 6. *Selected geometric parameters (Å, °) for (III)*

(*a*) Bonds lengths, angles and torsions

P—O1	1.551 (2)	K—O4	2.826 (2)
P—O2	1.527 (2)	K—O3	2.860 (2)
P—O3	1.500 (2)	K—O2^{iii}	2.888 (2)
P—C2	1.812 (2)	K—O6^{iv}	2.900 (2)
C2—C1	1.502 (2)	K—O2^{v}	3.062 (2)
C1—O4	1.319 (2)	K—O4^{vi}	3.100 (2)
C1—O5	1.213 (2)	K—O1^{iv}	3.419 (2)
K—O6^{i}	2.813 (2)	K···K^{vi}	4.472 (2)
K—O5^{ii}	2.818 (2)		
O1—P—O2	110.1 (1)	O3—P—C2	107.5 (1)
O1—P—O3	110.6 (1)	C1—C2—P	112.6 (2)
O2—P—O3	114.1 (1)	O4—C1—C2	113.5 (2)
O1—P—C2	107.0 (1)	O5—C1—C2	123.5 (2)
O2—P—C2	107.2 (1)	O5—C1—O4	122.9 (2)
O1—P—C2—C1	63.1 (2)	P—C2—C1—O4	97.6 (2)
O2—P—C2—C1	−178.7 (2)	P—C2—C1—O5	−81.4 (2)
O3—P—C2—C1	−55.6 (2)		

Symmetry codes: (i) $x-1, \frac{3}{2}-y, z-\frac{1}{2}$; (ii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $1-x, 1-y, 1-z$; (iv) $x-1, y, z$; (v) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (vi) $x, \frac{3}{2}-y, z-\frac{1}{2}$.

(*b*) Hydrogen-bonding geometry

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^{i}	0.71 (4)	1.90 (4)	2.597 (2)	169 (4)
O4—H4···O3^{ii}	0.82 (6)	1.73 (5)	2.537 (2)	168 (6)
O6—H61···O5	0.81 (4)	2.12 (4)	2.875 (3)	155 (4)
O6—H62···O1^{iii}	0.93 (5)	2.11 (5)	3.013 (2)	162 (4)

Symmetry codes: (i) $2-x, 1-y, 1-z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $2-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Compound (IV)

Crystal data

$NH_4^+.C_2H_4O_5P^-$
$M_r = 157.06$
Monoclinic
$P2_1/c$
$a = 6.812\ (4)$ Å
$b = 10.258\ (4)$ Å
$c = 9.285\ (4)$ Å
$\beta = 100.84\ (4)°$
$V = 637.2\ (6)$ Å^3
$Z = 4$
$D_x = 1.637\ (2)$ Mg m^{-3}
$D_m = 1.62$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 31 reflections
$\theta = 10–13°$
$\mu = 0.389$ mm^{-1}
$T = 303\ (1)$ K
Large block
0.5 × 0.4 × 0.2 mm
Colorless

Data collection

Kuma KM-4 automatic diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3254 measured reflections
2356 independent reflections
1576 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0266$
$\theta_{max} = 35°$
$h = -10 \rightarrow 5$
$k = 0 \rightarrow 14$
$l = -13 \rightarrow 14$
3 standard reflections monitored every 100 reflections
intensity decay: 3%

Refinement

Refinement on F^2
$R(F) = 0.0293$
$wR(F^2) = 0.0768$
$S = 1.104$
2163 reflections
115 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 0.016P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.173$

$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.057 (5)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 7. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (IV)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
P	0.25782 (4)	0.56790 (3)	0.62304 (4)	0.0244 (1)
O1	0.05478 (14)	0.61241 (10)	0.66071 (12)	0.0350 (3)
O2	0.23217 (13)	0.43651 (8)	0.54593 (11)	0.0320 (2)
O3	0.41693 (14)	0.57030 (9)	0.75818 (11)	0.0344 (2)
O4	0.52968 (13)	0.84763 (10)	0.60861 (12)	0.0355 (3)
O5	0.20439 (15)	0.89343 (10)	0.55585 (14)	0.0432 (3)
C1	0.3417 (2)	0.81948 (12)	0.55363 (14)	0.0276 (3)
C2	0.3161 (2)	0.68429 (12)	0.49108 (14)	0.0269 (3)
N	0.2003 (2)	0.16871 (13)	0.6316 (2)	0.0361 (3)

Table 8. *Selected geometric parameters (Å, °) for (IV)*

(*a*) Bonds lengths, angles and torsions

P—O1	1.557 (2)	C1—C2	1.501 (2)
P—O2	1.521 (2)	O4—C1	1.318 (2)
P—O3	1.496 (2)	O5—C1	1.208 (2)
P—C2	1.808 (2)		
O1—P—O2	109.7 (1)	O3—P—C2	109.9 (1)
O1—P—O3	109.9 (1)	C1—C2—P	111.9 (1)
O2—P—O3	114.2 (1)	O5—C1—O4	123.7 (2)
O1—P—C2	106.0 (1)	O5—C1—C2	123.6 (2)
O2—P—C2	106.7 (1)	O4—C1—C2	112.7 (1)
O1—P—C2—C1	62.1 (1)	O4—C1—C2—P	94.0 (2)
O2—P—C2—C1	179.0 (1)	O5—C1—C2—P	−84.6 (2)
O3—P—C2—C1	−56.6 (1)		

(*b*) Hydrogen-bonding geometry

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^{i}	0.70 (3)	1.82 (4)	2.519 (2)	178 (4)
O4—H4···O3^{ii}	0.82 (3)	1.79 (3)	2.590 (2)	166 (3)
N—H11···O1^{iii}	0.89 (3)	2.01 (3)	2.886 (3)	167 (3)
N—H12···O2	0.90 (3)	1.99 (3)	2.880 (2)	171 (3)
N—H13···O3^{iv}	0.82 (3)	2.03 (4)	2.804 (2)	157 (3)
N—H14···O5^{v}	0.76 (3)	2.48 (3)	2.912 (2)	118 (3)
N—H14···O5^{i}	0.76 (3)	2.51 (3)	3.038 (2)	128 (3)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iii) $-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iv) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; (v) $x, y-1, z$.

Compound (V)

Crystal data

$Li^+.C_2H_4O_5P^-$
$M_r = 145.96$
Monoclinic
$P2_1/c$
$a = 6.516$ (3) Å
$b = 10.596$ (4) Å
$c = 7.348$ (3) Å
$\beta = 95.82$ (4)°
$V = 504.7$ (4) Å^3
$Z = 4$
$D_x = 1.921$ (2) Mg m^{-3}
$D_m = 1.90$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–15°
$\mu = 0.476$ mm^{-1}
$T = 297$ (2) K
Column
0.4 × 0.2 × 0.2 mm
Colorless

Data collection

Kuma KM-4 automatic diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1543 measured reflections
1427 independent reflections
1216 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0151$
$\theta_{max} = 30°$
$h = -9 \rightarrow 1$
$k = 0 \rightarrow 14$
$l = -10 \rightarrow 10$
3 standard reflections monitored every 100 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R(F) = 0.0240$
$wR(F^2) = 0.0702$
$S = 1.101$
1376 reflections
99 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.042P)^2 + 0.18P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.148$

$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.027 (4)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 9. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (V)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
P	0.13626 (5)	0.58505 (3)	0.23907 (4)	0.01255 (11)
O1	0.13106 (14)	0.61267 (9)	0.43882 (12)	0.0172 (2)
O2	−0.02787 (14)	0.64799 (8)	0.11059 (12)	0.0166 (2)
O3	0.1198 (2)	0.43672 (9)	0.21676 (13)	0.0182 (2)
O4	0.6113 (2)	0.47388 (10)	0.2912 (2)	0.0254 (2)
O5	0.6475 (2)	0.66681 (10)	0.41280 (15)	0.0260 (3)
C1	0.5616 (2)	0.59389 (12)	0.3027 (2)	0.0175 (3)
C2	0.3835 (2)	0.63167 (13)	0.1686 (2)	0.0183 (3)
Li	0.0961 (4)	0.3234 (2)	0.4333 (3)	0.0197 (5)

Table 10. *Selected geometric parameters (Å, °) for (V)*

(*a*) Bonds lengths, angles and torsions

P—O1	1.500 (2)	O5—C1	1.214 (2)
P—O2	1.508 (2)	Li—O1^{i}	1.954 (3)
P—O3	1.583 (2)	Li—O2^{ii}	1.930 (2)
P—C2	1.810 (2)	Li—O3	2.012 (3)
C1—C2	1.499 (2)	Li—O5^{iii}	1.923 (3)
O4—C1	1.317 (2)		
O1—P—O2	116.2 (1)	O3—P—C2	107.1 (1)
O1—P—O3	106.7 (1)	C1—C2—P	113.0 (1)
O2—P—O3	109.7 (1)	O5—C1—C2	122.8 (2)
O1—P—C2	109.6 (1)	O4—C1—C2	113.3 (2)
O2—P—C2	107.2 (1)	O5—C1—O4	123.9 (2)
O1—P—C2—C1	43.4 (2)	O4—C1—C2—P	78.5 (2)
O2—P—C2—C1	170.3 (1)	O5—C1—C2—P	−100.0 (2)
O3—P—C2—C1	−71.9 (2)		

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $1-x, 1-y, 1-z$.

(*b*) Hydrogen-bonding geometry

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2^{i}	0.74 (3)	1.84 (3)	2.580 (2)	179 (3)
O4—H4···O1^{ii}	0.77 (3)	1.86 (3)	2.630 (2)	177 (3)

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $1-x, 1-y, 1-z$.

Compound (VI)

Crystal data

$Na^+.C_2H_4O_5P^-.2H_2O$
$M_r = 198.04$
Orthorhombic
$Pca2_1$
$a = 5.806$ (2) Å
$b = 17.430$ (6) Å
$c = 14.607$ (5) Å
$V = 1478.2$ (9) Å^3
$Z = 8$
$D_x = 1.780$ (2) Mg m^{-3}
$D_m = 1.79$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 10$–17°
$\mu = 3.969$ mm^{-1}
$T = 295$ (1) K
Needle
0.40 × 0.15 × 0.08 mm
Colorless

Data collection

Kuma KM-4 automatic diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (see *Experimental* text)
$T_{min} = 0.36$, $T_{max} = 0.75$
5939 measured reflections
2957 independent reflections
2726 observed reflections $[I > 2\sigma(I)]$

$R_{int} = 0.0662$
$\theta_{max} = 80°$
$h = -7 \rightarrow 1$
$k = -22 \rightarrow 22$
$l = -18 \rightarrow 18$
2 standard reflections monitored every 50 reflections
intensity decay: 9%

Refinement

Refinement on F^2
$R(F) = 0.0378$
$wR(F^2) = 0.1026$
$S = 1.107$
2957 reflections
262 parameters
All H-atom parameters refined

$\Delta\rho_{max} = 0.84$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

$w = 1/[\sigma^2(F_o^2) + (0.074P)^2 + 0.08P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.157$

Absolute configuration: Flack (1983)
Flack parameter = 0.00 (2)

Table 11. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (VI)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Na1	0.6087 (2)	0.43721 (6)	0.57590 (9)	0.0289 (3)
Na2	0.6173 (2)	0.05636 (6)	0.31232 (9)	0.0279 (3)
P1A	0.36352 (9)	0.32409 (3)	0.4	0.0194 (2)
P1B	0.14645 (9)	0.17382 (3)	0.63058 (5)	0.0196 (2)
O1A	0.4126 (4)	0.33343 (11)	0.50551 (13)	0.0265 (4)
O2A	0.4024 (4)	0.24307 (11)	0.3707 (2)	0.0313 (5)
O3A	0.5053 (4)	0.38375 (10)	0.35173 (15)	0.0291 (4)
O4A	0.0403 (4)	0.47248 (11)	0.33513 (15)	0.0280 (4)
O5A	−0.0561 (4)	0.45254 (12)	0.48062 (14)	0.0307 (4)
C1A	0.0059 (4)	0.42822 (13)	0.4064 (2)	0.0220 (5)
C2A	0.0591 (5)	0.34534 (15)	0.3868 (2)	0.0270 (5)
O1B	0.0596 (4)	0.15935 (11)	0.73083 (14)	0.0295 (4)
O2B	0.1289 (4)	0.25722 (11)	0.60592 (15)	0.0302 (5)
O3B	0.0185 (4)	0.11851 (11)	0.56992 (15)	0.0278 (4)
O4B	0.4612 (4)	0.02601 (11)	0.56711 (14)	0.0292 (4)
O5B	0.5652 (4)	0.03814 (12)	0.71304 (15)	0.0295 (4)
C1B	0.4990 (4)	0.06657 (14)	0.6418 (2)	0.0221 (5)
C2B	0.4520 (5)	0.14999 (15)	0.6292 (3)	0.0300 (6)
O6	0.2521 (5)	0.05497 (12)	0.3895 (2)	0.0311 (4)
O7	0.2473 (4)	0.45269 (12)	0.1567 (2)	0.0315 (4)
O8	0.6863 (6)	0.3583 (2)	0.1755 (2)	0.0507 (7)
O9	−0.2008 (5)	0.14901 (14)	0.4032 (2)	0.0423 (6)

Table 12. *Selected geometric parameters (Å, °) for (VI)*

(*a*) Bonds lengths, angles and torsions

P1A—O1A	1.576 (2)	O5B—C1B	1.215 (3)
P1A—O2A	1.493 (2)	Na1—O1A	2.372 (2)
P1A—O3A	1.502 (2)	Na1—O5A^{i}	2.407 (2)
P1A—C2A	1.816 (3)	Na1—O5A^{ii}	2.558 (2)
C1A—C2A	1.505 (3)	Na1—O8^{iii}	2.329 (3)
O4A—C1A	1.312 (3)	Na1—O7^{iv}	2.396 (2)
O5A—C1A	1.218 (3)	Na1—O7^{v}	2.403 (2)
P1B—O1B	1.569 (2)	Na2—O1B^{vi}	2.386 (2)
P1B—O2B	1.501 (2)	Na2—O5B^{vii}	2.367 (2)
P1B—O3B	1.505 (2)	Na2—O5B^{viii}	2.437 (2)
P1B—C2B	1.822 (3)	Na2—O6^{ix}	2.377 (2)
C1B—C2B	1.491 (3)	Na2—O6	2.402 (3)
O4B—C1B	1.319 (3)	Na2—O9^{i}	2.342 (3)
O1A—P1A—O2A	110.5 (2)	O1B—P1B—O2B	111.0 (2)
O1A—P1A—O3A	106.8 (2)	O1B—P1B—O3B	106.7 (2)
O2A—P1A—O3A	115.9 (2)	O2B—P1B—O3B	116.5 (2)
O1A—P1A—C2A	105.0 (2)	O1B—P1B—C2B	106.6 (2)
O2A—P1A—C2A	108.0 (2)	O2B—P1B—C2B	106.5 (2)
O3A—P1A—C2A	110.0 (2)	O3B—P1B—C2B	109.1 (2)
C1A—C2A—P1A	112.0 (2)	C1B—C2B—P1B	113.5 (2)
O4A—C1A—C2A	112.4 (2)	O4B—C1B—C2B	113.0 (2)
O5A—C1A—C2A	124.4 (3)	O5B—C1B—C2B	124.2 (2)
O5A—C1A—O4A	123.1 (2)	O5B—C1B—O4B	122.9 (2)
O1A—P1A—C2A—C1A	67.3 (2)	O1B—P1B—C2B—C1B	68.1 (2)
O2A—P1A—C2A—C1A	−174.7 (2)	O2B—P1B—C2B—C1B	−173.3 (2)
O3A—P1A—C2A—C1A	−47.3 (2)	O3B—P1B—C2B—C1B	−46.8 (2)
O4A—C1A—C2A—P1A	84.2 (2)	O4B—C1B—C2B—P1B	77.2 (3)
O5A—C1A—C2A—P1A	−93.9 (3)	O5B—C1B—C2B—P1B	−102.8 (3)

Symmetry codes: (i) $1+x, y, z$; (ii) $\frac{1}{2}+x, 1-y, z$; (iii) $\frac{3}{2}-x, y, \frac{1}{2}+z$; (iv) $\frac{1}{2}-x, y, \frac{1}{2}+z$; (v) $1-x, 1-y, \frac{1}{2}+z$; (vi) $\frac{1}{2}-x, y, z-\frac{1}{2}$; (vii) $\frac{3}{2}-x, y, z-\frac{1}{2}$; (viii) $1-x, -y, z-\frac{1}{2}$; (ix) $\frac{1}{2}+x, -y, z$.

(*b*) Hydrogen-bonding geometry

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1A—H1A···O2B	0.88 (5)	1.70 (5)	2.575 (3)	169 (5)
O4A—H4A···O3A^{i}	0.82 (7)	1.73 (7)	2.526 (3)	166 (7)
O1B—H1B···O2A^{ii}	0.74 (9)	1.82 (9)	2.520 (3)	156 (9)
O4B—H4B···O3B^{iii}	0.99 (5)	1.61 (5)	2.541 (3)	155 (5)

O6—H6···O4*B*	0.93 (7)	2.00 (7)	2.908 (3)	167 (6)
O6—H61···O9	0.70 (7)	2.50 (7)	3.105 (4)	146 (7)
O7—H7···O4*A*	0.95 (5)	1.97 (6)	2.890 (3)	164 (5)
O7—H71···O8	0.88 (9)	2.18 (9)	3.046 (4)	172 (8)
O8—H8···O3*A*	0.99 (7)	1.85 (7)	2.816 (3)	165 (5)
O8—H81···O2B^{iv}	0.75 (5)	2.04 (5)	2.736 (3)	156 (6)
O9—H9···O3*B*	0.90 (7)	1.92 (7)	2.799 (3)	166 (6)
O9—H91···O2A^{v}	0.91 (6)	2.03 (6)	2.867 (3)	152 (5)

Symmetry codes: (i) $x-\frac{1}{2}, 1-y, z$; (ii) $\frac{1}{2}-x, y, \frac{1}{2}+z$; (iii) $\frac{1}{2}+x, -y, z$; (iv) $\frac{1}{2}-x, y, z-\frac{1}{2}$; (v) $x-1, y, z$.

Compound (VII)

Crystal data

$2K^+.C_2H_3O_5P^{2-}$
$M_r = 216.21$
Monoclinic
$P2_1/c$
$a = 9.260\ (4)$ Å
$b = 10.163\ (4)$ Å
$c = 6.885\ (4)$ Å
$\beta = 95.95\ (4)°$
$V = 644.5\ (5)$ Å^3
$Z = 4$
$D_x = 2.228$ Mg m^{-3}
$D_m = 2.23$ Mg m^{-3}

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 73 reflections
$\theta = 10$–$20°$
$\mu = 1.674$ mm^{-1}
$T = 150\ (2)$ K
Block
0.3 × 0.3 × 0.3 mm
Colorless

Data collection

Kuma KM-4 automatic diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2060 measured reflections
1866 independent reflections
1364 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0204$
$\theta_{max} = 30°$
$h = -13 \rightarrow 12$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 9$
3 standard reflections monitored every 100 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.0272$
$wR(F^2) = 0.0731$
$S = 1.085$
1866 reflections
103 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 0.35P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.061$
$\Delta\rho_{max} = 0.59$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 13. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (VII)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
P	0.71562 (5)	0.46028 (5)	0.66964 (8)	0.0092 (2)
O1	0.7175 (2)	0.60794 (15)	0.6948 (3)	0.0139 (3)
O2	0.6008 (2)	0.38449 (16)	0.7595 (3)	0.0155 (3)
O3	0.8706 (2)	0.40375 (14)	0.7502 (3)	0.0124 (3)
O4	0.9320 (2)	0.42800 (14)	0.2996 (3)	0.0131 (3)
O5	0.7867 (2)	0.60000 (15)	0.2296 (3)	0.0151 (3)
C1	0.8116 (3)	0.4882 (2)	0.3028 (4)	0.0100 (3)
C2	0.6973 (3)	0.4218 (2)	0.4095 (4)	0.0103 (4)
K1	0.43317 (5)	0.20399 (4)	0.52224 (7)	0.0138 (2)
K2	0.95003 (5)	0.77537 (4)	0.46557 (6)	0.0132 (2)

Table 14. *Selected geometric parameters (Å, °) for (VII)*

(*a*) Bonds lengths, angles and torsions

P—O1	1.511 (2)	K1—O1^{iii}	2.694 (2)
P—O2	1.497 (2)	K1—O1^{iv}	2.721 (2)
P—O3	1.592 (2)	K1—O5^{v}	2.745 (2)
P—C2	1.824 (2)	K1—O5^{iv}	3.428 (2)
C1—C2	1.509 (3)	K2—O4^{vi}	2.710 (2)
O4—C1	1.274 (2)	K2—O1	3.275 (2)
O5—C1	1.255 (2)	K2—O3^{vii}	2.760 (2)
K2—O3^{i}	2.965 (2)	K2—O5^{viii}	2.787 (2)
K2—O4^{i}	2.777 (2)	K2—O5	2.756 (2)
K1—O2^{ii}	2.660 (2)	K2—O1^{ix}	2.947 (2)
K1—O2	2.814 (2)		
O1—P—O2	117.6 (1)	O3—P—C2	104.7 (1)
O1—P—O3	108.6 (1)	C1—C2—P	112.6 (2)
O2—P—O3	108.9 (1)	O4—C1—C2	117.0 (2)
O1—P—C2	108.9 (1)	O5—C1—C2	119.5 (2)
O2—P—C2	107.3 (1)	O5—C1—O4	123.5 (2)
O1—P—C2—C1	54.0 (2)	O4—C1—C2—P	86.7 (2)
O2—P—C2—C1	−177.6 (2)	O5—C1—C2—P	−90.4 (2)
O3—P—C2—C1	−62.0 (2)		

Symmetry codes: (i) $2-x, 1-y, 1-z$; (ii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iv) $1-x, 1-y, 1-z$; (v) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (vi) $2-x, \frac{1}{2}+y, \frac{1}{2}-z$; (vii) $2-x, \frac{1}{2}+y, \frac{3}{2}-z$; (viii) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (ix) $x, \frac{3}{2}-y, z-\frac{1}{2}$.

(*b*) Hydrogen-bonding geometry

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O4^{i}	0.91 (5)	1.66 (5)	2.551 (2)	165 (5)

Symmetry code: (i) $2-x, 1-y, 1-z$.

Compound (VIII)

Crystal data

$2NH_4^+.C_2H_3O_5P^{2-}$
$M_r = 174.10$
Monoclinic
$P2_1/c$
$a = 9.568\ (7)$ Å
$b = 10.407\ (9)$ Å
$c = 7.087\ (6)$ Å
$\beta = 93.89\ (7)°$
$V = 704.1\ (10)$ Å^3
$Z = 4$
$D_x = 1.642\ (3)$ Mg m^{-3}
$D_m = 1.623$ Mg m^{-3}

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 73 reflections
$\theta = 9$–$12°$
$\mu = 0.364$ mm^{-1}
$T = 150\ (2)$ K
Large block
0.7 × 0.5 × 0.4 mm
Colorless

Data collection

Kuma KM-4 automatic diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1750 measured reflections
1652 independent reflections
1492 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0329$
$\theta_{max} = 30°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 14$
$l = -9 \rightarrow 9$
3 standard reflections monitored every 100 reflections intensity decay: 5%

Refinement

Refinement on F^2
$R(F) = 0.0352$
$wR(F^2) = 0.0928$
$S = 1.123$

$(\Delta/\sigma)_{max} = 0.099$
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}
Extinction correction: none

1610 reflections
135 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 0.17P]$
where $P = (F_o^2 + 2F_c^2)/3$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 15. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (VIII)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
P	0.71832 (3)	0.45949 (3)	0.66623 (4)	0.0091 (2)
O1	0.71877 (10)	0.60317 (9)	0.69181 (13)	0.0131 (3)
O2	0.60652 (10)	0.38501 (10)	0.75680 (13)	0.0151 (3)
O3	0.86572 (10)	0.40379 (9)	0.74022 (13)	0.0138 (3)
O4	0.92890 (10)	0.43331 (9)	0.29683 (14)	0.0139 (3)
O5	0.78431 (10)	0.59854 (9)	0.23840 (13)	0.0146 (3)
C1	0.81117 (14)	0.48926 (12)	0.3066 (2)	0.0104 (3)
C2	0.70156 (13)	0.42244 (12)	0.4146 (2)	0.0112 (3)
N1	0.43822 (13)	0.21651 (11)	0.5332 (2)	0.0130 (3)
N2	0.94581 (13)	0.77476 (11)	0.4801 (2)	0.0130 (3)

Table 16. *Selected geometric parameters (Å, °) for (VIII)*

(*a*) Bonds lengths, angles and torsions

P—O1	1.506 (2)	C1—C2	1.509 (2)
P—O2	1.500 (2)	O4—C1	1.274 (2)
P—O3	1.581 (2)	O5—C1	1.255 (2)
P—C2	1.821 (2)		
O1—P—O2	117.2 (1)	O3—P—C2	105.3 (1)
O1—P—O3	109.2 (1)	C1—C2—P	112.4 (1)
O2—P—O3	108.3 (1)	O4—C1—C2	117.7 (2)
O1—P—C2	109.1 (1)	O5—C1—C2	118.8 (2)
O2—P—C2	107.0 (1)	O5—C1—O4	123.5 (2)
O1—P—C2—C1	53.7 (2)	O4—C1—C2—P	86.7 (2)
O2—P—C2—C1	−178.6 (1)	O5—C1—C2—P	−90.3 (2)
O3—P—C2—C1	−63.4 (2)		

(*b*) Hydrogen-bonding geometry

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O4^{i}	0.78 (3)	1.84 (3)	2.622 (2)	177 (3)
N1—H11···O2^{ii}	0.89 (2)	1.97 (3)	2.824 (2)	159 (2)
N1—H12···O1^{iii}	0.85 (2)	1.97 (3)	2.801 (2)	163 (2)
N1—H13···O2	0.91 (2)	1.89 (3)	2.799 (2)	174 (3)
N1—H14···O1^{iv}	0.91 (2)	1.93 (3)	2.828 (3)	170 (3)
N2—H21···O4^{v}	0.87 (2)	2.04 (3)	2.886 (2)	165 (3)
N2—H22···O5^{vi}	0.89 (2)	1.92 (3)	2.804 (2)	171 (3)
N2—H23···O4^{i}	0.90 (2)	2.00 (3)	2.893 (2)	169 (3)
N2—H24···O5	0.85 (2)	2.04 (3)	2.885 (2)	171 (3)

Symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iv) $1 - x, 1 - y, 1 - z$; (v) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vi) $x, \frac{3}{2} - y, \frac{1}{2} + z$.

Compound (IX)

Crystal data

$2Na^+.C_2H_3O_5P^{2-}.2H_2O$
$M_r = 220.03$
Monoclinic
$C2/c$
$a = 11.76$ (2) Å
$b = 6.780$ (4) Å
$c = 19.64$ (2) Å
$\beta = 101.42$ (9)°
$V = 1535$ (4) Å^3
$Z = 8$
$D_x = 1.904$ (4) Mg m^{-3}
$D_m = 1.897$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 10$–13°
$\mu = 0.467$ mm^{-1}
$T = 297$ (1) K
Long plate
0.6 × 0.4 × 0.2 mm
Colorless

Data collection

Kuma KM-4 automatic diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2263 measured reflections
2250 independent reflections
1615 observed reflections
$[I > 2\sigma(I)]$

$R_{int} = 0.0125$
$\theta_{max} = 35°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 10$
$l = -31 \rightarrow 30$
3 standard reflections monitored every 100 reflections
intensity decay: 5%

Refinement

Refinement on F^2
$R(F) = 0.0513$
$wR(F^2) = 0.1371$
$S = 1.104$
2250 reflections
146 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.118P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.092$
$\Delta\rho_{max} = 0.78$ e Å^{-3}
$\Delta\rho_{min} = -1.15$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 17. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (IX)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
P	0.65227 (5)	0.27093 (8)	0.60797 (3)	0.0151 (2)
O1	0.60325 (15)	0.4419 (2)	0.56277 (8)	0.0194 (4)
O2	0.74526 (15)	0.3167 (3)	0.66999 (9)	0.0236 (4)
O3	0.70230 (15)	0.1129 (2)	0.56121 (9)	0.0193 (4)
O4	0.4424 (2)	−0.0959 (2)	0.55550 (9)	0.0248 (4)
O5	0.3686 (2)	0.2056 (3)	0.55081 (9)	0.0227 (4)
O6	0.7566 (3)	0.7246 (4)	0.69188 (12)	0.0512 (8)
O7†	0.9149 (5)	0.0416 (9)	0.6846 (4)	0.034 (2)
O71†	0.9545 (7)	0.1192 (14)	0.6804 (4)	0.055 (2)
C1	0.4406 (2)	0.0791 (3)	0.57778 (11)	0.0173 (5)
C2	0.5368 (2)	0.1402 (3)	0.63761 (11)	0.0179 (4)
Na1	0.91315 (9)	0.05519 (13)	0.56248 (5)	0.0219 (3)
Na2	0.17839 (10)	0.25864 (14)	0.57435 (5)	0.0269 (3)

† Site occupancy = 0.50.

Table 18. *Selected geometric parameters (Å, °) for (IX)*

(*a*) Bonds lengths, angles and torsions

P—O1	1.504 (2)	C2—C1	1.519 (3)
P—O2	1.499 (2)	O4—C1	1.267 (3)
P—O3	1.597 (2)	O5—C1	1.247 (3)
P—C2	1.811 (3)		
O1—P—O2	116.9 (2)	O3—P—C2	104.0 (2)
O1—P—O3	108.6 (2)	C1—C2—P	112.1 (2)
O2—P—O3	108.3 (2)	O4—C1—C2	117.5 (2)
O1—P—C2	110.0 (2)	O5—C1—C2	118.7 (2)
O2—P—C2	108.2 (2)	O5—C1—O4	123.6 (2)
O1—P—C2—C1	53.7 (2)	P—C2—C1—O4	97.6 (3)
O2—P—C2—C1	−177.4 (2)	P—C2—C1—O5	−78.3 (3)
O3—P—C2—C1	−62.5 (2)		

(*b*) Hydrogen-bonding geometry

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O4^{i}	0.84 (5)	1.75 (5)	2.572 (4)	166 (5)
O3—H3···O5^{i}	0.84 (5)	2.46 (4)	3.078 (4)	132 (4)
O6—H6···O2	0.80 (5)	2.02 (5)	2.798 (4)	162 (4)
O6—H61···O2^{ii}	0.90 (9)	2.09 (9)	2.788 (4)	133 (8)
O7—H7···O2	1.04 (7)	1.81 (7)	2.705 (7)	142 (6)
O71—H7···O2	0.97 (7)	1.81 (7)	2.774 (8)	176 (6)

O7—H71···O7^{iii}	1.02 (7)	2.29 (6)	2.929 (13)	119 (6)
O7—H71···O71^{iii}	1.02 (7)	2.20 (6)	2.839 (7)	119 (6)
O71—H7···O7^{iii}	0.57 (7)	2.29 (6)	2.839 (7)	162 (10)
O71—H71···O71^{iii}	0.57 (7)	2.20 (6)	2.733 (14)	157 (10)

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $2 - x, y, \frac{3}{2} - z$.

Compound (X)

Crystal data

$3NH_4^+.C_2H_2O_5P^{3-}.2H_2O$
$M_r = 227.16$
Monoclinic
$P2_1/n$
$a = 6.883$ (6) Å
$b = 10.982$ (9) Å
$c = 14.148$ (9) Å
$\beta = 90.19$ (6)°
$V = 1069.4$ (15) Å^3
$Z = 4$
$D_x = 1.411$ (3) Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 58 reflections
$\theta = 9$–13°
$\mu = 0.273$ mm^{-1}
$T = 150$ (1) K
Block
0.50 × 0.25 × 0.20 mm
Colorless

Data collection

Kuma KM-4 automatic diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3255 measured reflections
3034 independent reflections
2159 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0207$
$\theta_{max} = 30°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 15$
$l = -19 \rightarrow 19$
3 standard reflections monitored every 100 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R(F) = 0.0284$
$wR(F^2) = 0.0771$
$S = 1.140$
3034 reflections
190 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 0.11P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.176$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 19. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (X)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
P	0.64131 (4)	0.21600 (3)	0.36892 (2)	0.0104 (1)
O1	0.76629 (14)	0.28378 (9)	0.29784 (7)	0.0168 (2)
O2	0.76178 (13)	0.12975 (8)	0.43069 (6)	0.0146 (2)
O3	0.47168 (13)	0.14965 (9)	0.32192 (7)	0.0162 (2)
O4	0.24297 (15)	0.40761 (10)	0.38940 (8)	0.0224 (3)
O5	0.51349 (15)	0.50942 (9)	0.35616 (7)	0.0189 (2)
O6	0.0622 (2)	0.25626 (10)	0.50606 (8)	0.0210 (2)
O7	0.6916 (2)	0.06596 (10)	0.61662 (7)	0.0213 (3)
C1	0.4237 (2)	0.42332 (11)	0.39473 (9)	0.0136 (3)
C2	0.5421 (2)	0.32946 (11)	0.44856 (9)	0.0132 (3)
N1	0.3771 (2)	0.72081 (11)	0.26900 (8)	0.0158 (2)
N2	0.5772 (2)	0.05607 (11)	0.14703 (9)	0.0173 (2)
N3	0.6085 (2)	0.41588 (11)	0.14873 (9)	0.0178 (2)

Table 20. *Selected geometric parameters (Å, °) for (X)*

(*a*) Bonds lengths, angles and torsions

P—O1	1.520 (2)	C2 C1	1.518 (2)
P—O2	1.531 (2)	O4—C1	1.258 (2)
P—O3	1.527 (2)	O5—C1	1.256 (2)
P—C2	1.815 (2)		
O1—P—O2	112.0 (1)	O3—P—C2	108.0 (1)
O1—P—O3	112.3 (1)	C1—C2—P	110.9 (1)
O2—P—O3	111.4 (1)	O4—C1—C2	117.8 (2)
O1—P—C2	106.8 (1)	O5—C1—C2	117.7 (2)
O2—P—C2	105.9 (1)	O5—C1—O4	124.4 (2)
O1—P—C2—C1	58.8 (2)	P—C2—C1—O4	95.3 (2)
O2—P—C2—C1	178.3 (1)	P—C2—C1—O5	−82.6 (2)
O3—P—C2—C1	−62.2 (2)		

(*b*) Hydrogen-bonding geometry

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O7^{i}	0.87 (3)	2.02 (3)	2.886 (2)	174 (2)
N1—H12···O5	1.01 (3)	1.82 (3)	2.790 (2)	160 (2)
N1—H13···O3^{ii}	0.90 (3)	1.95 (3)	2.830 (3)	166 (2)
N1—H14···O1^{iii}	0.86 (3)	1.88 (3)	2.723 (3)	166 (2)
N2—H21···O6^{iv}	0.88 (3)	1.99 (3)	2.870 (3)	171 (3)
N2—H22···O3	0.86 (3)	1.93 (3)	2.778 (2)	169 (2)
N2—H23···O4^{v}	0.83 (3)	1.96 (3)	2.788 (2)	169 (2)
N2—H24···O5^{vi}	0.88 (3)	2.02 (3)	2.864 (3)	162 (3)
N3—H31···O6^{iv}	0.89 (3)	1.92 (3)	2.783 (2)	165 (2)
N3—H32···O1	0.94 (3)	1.85 (3)	2.778 (2)	164 (3)
N3—H33···O2^{iii}	0.93 (3)	1.85 (3)	2.754 (2)	165 (3)
N3—H34···O7^{vii}	0.89 (3)	2.10 (3)	2.911 (3)	152 (2)
O6—H6···O2^{viii}	0.79 (3)	1.92 (3)	2.707 (2)	172 (3)
O6—H61···O4	0.75 (3)	1.92 (3)	2.655 (2)	169 (3)
O7—H7···O2	0.83 (3)	1.95 (3)	2.766 (2)	167 (3)
O7—H71···O3^{ix}	0.83 (3)	1.93 (3)	2.763 (2)	173 (3)

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$; (v) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (vi) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (vii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (viii) $x - 1, y, z$; (ix) $1 - x, -y, 1 - z$.

Compound (XI)

Crystal data

$3Na^+.C_2H_2O_5P^{3-}.10H_2O$
$M_r = 386.14$
Monoclinic
$P2_1/m$
$a = 7.891$ (6) Å
$b = 24.846$ (17) Å
$c = 8.324$ (6) Å
$\beta = 101.46$ (6)°
$V = 1599$ (3) Å^3
$Z = 4$
$D_x = 1.604$ (3) Mg m^{-3}
$D_m = 1.615$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 10$–15°
$\mu = 0.321$ mm^{-1}
$T = 297$ (1) K
Block
0.6 × 0.6 × 0.2 mm
Colorless

Data collection

Kuma KM-4 automatic diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4464 measured reflections
4457 independent reflections
3277 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0154$
$\theta_{max} = 30°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 34$
$l = -11 \rightarrow 11$
3 standard reflections monitored every 50 reflections
intensity decay: 3%

Refinement

Refinement on F^2
$R(F) = 0.0372$
$wR(F^2) = 0.0922$
$S = 1.080$
4457 reflections
303 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.066P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.178$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.58$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 21. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (XI)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
P	0.30391 (5)	0.63037 (2)	0.35779 (4)	0.0170 (1)
O1	0.42258 (14)	0.66693 (5)	0.47632 (13)	0.0248 (3)
O2	0.40618 (15)	0.58910 (5)	0.27960 (13)	0.0248 (3)
O3	0.17975 (15)	0.66221 (5)	0.22847 (13)	0.0253 (3)
O4	−0.0643 (2)	0.64691 (5)	0.5143 (2)	0.0316 (3)
O5	0.1531 (2)	0.63867 (6)	0.72611 (14)	0.0350 (3)
C1	0.0823 (2)	0.62848 (6)	0.5806 (2)	0.0231 (3)
C2	0.1761 (3)	0.59260 (6)	0.4794 (2)	0.0247 (3)
Na1	0.29673 (8)	0.41084 (3)	0.04809 (8)	0.0263 (2)
Na2	0	1/2	0	0.0293 (3)
Na3	0.94048 (12)	3/4	0.52693 (12)	0.0293 (3)
Na4	0.65886 (12)	3/4	0.15307 (11)	0.0255 (2)
Na5†	0.2889 (2)	0.77438 (7)	0.8402 (2)	0.0341 (4)
O6	0.7002 (2)	0.65123 (5)	0.1888 (2)	0.0320 (3)
O7	0.2290 (2)	0.48606 (6)	0.8536 (2)	0.0353 (3)
O8	0.0055 (2)	0.59695 (5)	−0.0118 (2)	0.0284 (3)
O9	0.4086 (2)	0.58392 (6)	0.9420 (2)	0.0352 (3)
O10	0.6840 (2)	0.65128 (6)	0.7318 (2)	0.0342 (3)
O11	0.2537 (2)	0.48761 (6)	0.2200 (2)	0.0332 (3)
O12	0.7168 (2)	0.55174 (6)	0.4544 (2)	0.0341 (3)
O13	0.6458 (2)	3/4	0.4413 (2)	0.0247 (4)
O14	0.3475 (3)	3/4	0.1163 (3)	0.0298 (4)
O15	−0.0388 (3)	3/4	0.2262 (3)	0.0349 (4)
O16	0.6002 (3)	3/4	0.8679 (3)	0.0391 (5)
O17	0.2419 (3)	3/4	0.5712 (3)	0.0261 (4)
O18†	0.0100 (4)	0.73251 (14)	0.8224 (4)	0.0374 (7)

† Site occupancy = 0.50.

Table 22. *Selected geometric parameters (Å, °) for (XI)*

(*a*) Bonds lengths, angles and torsions

P—O1	1.519 (2)	C1—C2	1.517 (2)
P—O2	1.528 (2)	O4—C1	1.264 (2)
P—O3	1.525 (2)	O5—C1	1.255 (2)
P—C2	1.824 (2)		
O1—P—O2	111.6 (1)	O3—P—C2	108.1 (1)
O1—P—O3	112.0 (1)	C1—C2—P	113.0 (2)
O2—P—O3	111.5 (1)	O4—C1—C2	118.4 (2)
O1—P—C2	106.5 (1)	O5—C1—C2	118.8 (2)
O2—P—C2	106.7 (1)	O5—C1—O4	122.8 (2)
O1—P—C2—C1	54.1 (2)	O4—C1—C2—P	86.0 (2)
O2—P—C2—C1	173.5 (2)	O5—C1—C2—P	−93.9 (2)
O3—P—C2—C1	−66.4 (2)		

(*b*) Hydrogen-bonding geometry

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6···O4$^{\rm i}$	0.90 (4)	2.14 (4)	2.968 (2)	152 (3)
O6—H61···O2	0.94 (3)	2.07 (3)	3.006 (2)	173 (3)
O7—H7···O9	0.84 (3)	2.00 (3)	2.837 (2)	174 (3)
O7—H71···O12$^{\rm ii}$	0.81 (3)	2.04 (3)	2.841 (2)	173 (3)
O8—H8···O5$^{\rm iii}$	0.83 (3)	2.04 (3)	2.863 (3)	174 (3)
O8—H81···O3	0.74 (3)	1.99 (3)	2.725 (2)	172 (3)
O9—H9···O2$^{\rm iv}$	0.81 (3)	2.03 (3)	2.817 (3)	163 (3)
O9—H91···O5	0.81 (4)	1.97 (3)	2.776 (3)	171 (3)
O10—H10···O4$^{\rm i}$	0.79 (3)	2.18 (3)	2.944 (3)	162 (3)
O10—H101···O1	0.77 (3)	1.92 (3)	2.681 (3)	171 (3)
O11—H11···O12$^{\rm ii}$	0.78 (3)	2.07 (3)	2.847 (3)	179 (3)
O11—H111···O2	0.83 (3)	1.97 (3)	2.796 (3)	174 (3)
O12—H12···O4$^{\rm i}$	0.78 (3)	2.14 (4)	2.912 (3)	170 (3)
O12—H121···O2	0.81 (3)	1.96 (4)	2.751 (3)	167 (3)
O13—H13···O1	0.88 (3)	1.90 (3)	2.766 (2)	169 (3)
O14—H14···O3	0.93 (3)	1.87 (3)	2.806 (2)	179 (3)
O15—H15···O3	0.90 (3)	1.90 (3)	2.778 (3)	165 (3)
O16—H16···O10	0.76 (3)	2.08 (3)	2.835 (3)	168 (3)
O17—H17···O1	0.84 (3)	1.88 (3)	2.713 (3)	170 (3)
O18—H18···O5	0.71 (6)	2.11 (6)	2.777 (4)	157 (7)

Symmetry codes: (i) $1 + x, y, z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $x, y, z - 1$; (iv) $x, y, 1 + z$.

Table 23. *Comparison of* ϕ† *values (°)*

Compound	ϕ	Compound	ϕ
H_3AP		HAP^{2-}	
(I)	50.6(1)	(VII)	89.0(1)
H_2AP^-		(VIII)	88.7(1)
(II)	76.5(1)	(IX)	79.5(2)
(III)	81.5(1)	AP^{3-}	
(IV)	85.8(1)	(X)	84.3(1)
(V)	75.6(1)	(XI)	83.6(1)
(VI*a*)	86.9(2)	AND‡	85.3(2)
(VI*b*)	79.9(2)		

† ϕ is the angle between the carboxyl plane and the plane through O2, P and C2. ‡ AND = 2-amino-5-nitropyridinium phosphonoacetate (Pécaut & Masse, 1994).

In the case of compound (I), the absolute structure cannot be determined reliably since the value of the Flack parameter was 0.43 (8) and the refinement of the inverted structure gave $R = 0.0255$ and $wR = 0.0715$ values, which do not differ significantly from those observed. The disordered K1 site in compound (III) was introduced in order to explain a peak of 1.04 e Å^{-3} close (0.69 Å) to the K atom. Its introduction reduced the R value from 0.0386 to 0.0375. In compound (VI), although the true space group is $Pca2_1$, the data for $hk0$ planes are weak when $h + k$ are odd. This indicates that the structure approximates to space group $Pcan$. Consistent with this, the atomic coordinates (Table 11) for the two phosphonoacetate anions and O6–O9 are related by the pseudosymmetry operations $\frac{1}{2} - x$, $\frac{1}{2} - y$, $\frac{1}{4} + z$, which is broken significantly only by Na1 and Na2. The absorption correction for compound (VI) was performed using the *SHELX*76 program (Sheldrick, 1976); a convex polyhedron was used to approximate the true shape of the crystal specimen. For compound (IX), extreme values in the final difference synthesis are within 0.9 Å of the P atom.

For all compounds: data collection, cell refinement and data reduction: *Kuma KM-4 Software* (Kuma Diffraction, 1989). Program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1260). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Metal Complexes of *trans*-2,2,4,4-Tetrafluoro-1,3-di-*tert*-butyl-1,3-diphosphetane

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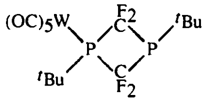
Abstract

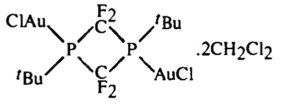
The title ligand, *L*, forms metal complexes $LW(CO)_5$ {pentacarbonyl(*trans*-1,3-di-*tert*-butyl-2,2,4,4-tetrafluoro-1,3-diphosphetane-*P*)tungsten, $[W(C_{10}H_{18}F_4P_2)(CO)_5]$, (1)} and $L(AuCl)_2.2CH_2Cl_2$ {μ-(*trans*-1,3-di-*tert*-butyl-2,2,4,4-tetrafluoro-1,3-diphosphetane-*P*:*P'*)-bis(chlorogold) dichloromethane solvate, $[Au_2Cl_2(C_{10}H_{18}F_4P_2)].2CH_2Cl_2$, (2)}. Complex (1) crystallizes with two independent but closely similar molecules; the P—W bond is short [2.482/2.488 (2) Å] and the P—C_{Bu} bonds are lengthened by *ca* 0.03 Å compared with those in the ligand disulfide, LS_2 [Fild, Jones, Ruhnau & Thöne (1994). *Z. Naturforsch. Teil B*, **49**, 1361–1367; the structure of *L* is not available for comparison]. The diphosphetane ring is folded by an angle of 21.4 (3)/22.0 (1)° about the C···C axis, in contrast with its exact planarity in both LS_2 and complex (2), which crystallizes with imposed *2/m* symmetry (*m* for the solvent); the Au—P bond is slightly shorter than the normal range at 2.212 (2) Å. Short contacts of 3.604 (2) Å are observed between the Au and solvent Cl atoms.

Comment

We reported recently the preparation of *trans*-2,2,4,4-tetrafluoro-1,3-di-*tert*-butyl-1,3-diphosphetane (hereafter *L*) (Fild, Jones, Ruhnau & Thöne, 1994). The structure of *L* was not determined (lack of suitable single crystals), but we were able to determine the structure of the disulfide, LS_2. Here, we extend our studies to the structure of two metal complexes of *L*, namely the tungsten, (I), and gold, (II), complexes.



(1)



(2)

Complex (1), $LW(CO)_5$ (Fig. 1), crystallizes with two independent molecules in the asymmetric unit. These molecules are related by a non-crystallographic glide plane. In contrast with the disulfide, LS_2, the central diphosphetane ring is not exactly planar; the fold angle about the C···C axis is 21.4 (3)/22.0 (1)°.

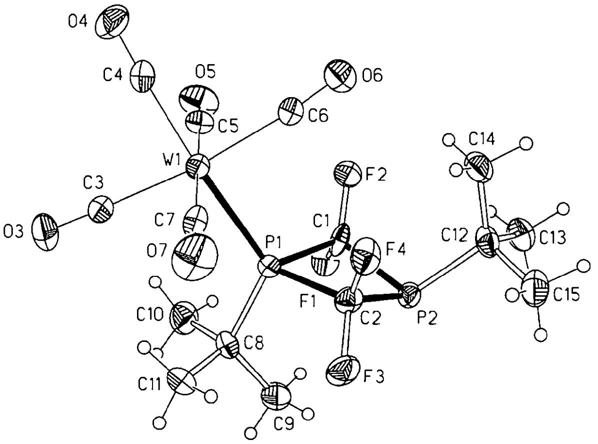


Fig. 1. One of the two independent molecules of (1) in the crystal. Ellipsoids correspond to 50% probability levels. H-atom radii are arbitrary.

Complex (2), $L(AuCl)_2.2CH_2Cl_2$ (Fig. 2), crystallizes with imposed *2/m* symmetry; atoms Au, Cl1, P, F, C2 and C3 lie in the mirror plane $(x,\frac{1}{2},z)$ (as do the solvent C and Cl atoms), and the C1 atom on the twofold axis $(\frac{1}{2},y,\frac{1}{2})$. The diphosphetane ring is thus exactly planar.

The corresponding diphenyl (rather than di-*tert*-butyl) ligand (Fild *et al.*, 1994) forms a bis[pentacarbonylchromium(0)] complex (Jones, 1996) in which the geometric consequences of complexation are easy to summarize: with respect to the free ligand, the P—CF_2 bonds are lengthened by *ca* 0.015 Å, whereas all other bond lengths and angles are scarcely altered. As indicated above, the structure of the current di-*tert*-butyl ligand, *L*, is unfortunately not available, only that of the corresponding disulfide, LS_2. Correspondingly, the results are less easy to interpret. Some effects of steric