

Table 4. Bond distances (Å) and angles (°) involving H atoms not included in Figs. 2 and 3

N(2)—H(2)	0.89 (7)	N(6)—H(7)	1.06 (6)
N(2)—H(3)	0.82 (6)	N(6)—H(8)	0.53 (7)
C(1)—N(2)—H(3)	118 (5)	C(3)—N(6)—H(7)	121 (4)
H(2)—N(2)—H(3)	122 (6)	C(3)—N(6)—H(8)	124 (7)
C(1)—N(2)—H(2)	120 (4)	H(7)—N(6)—H(8)	112 (8)
N(3)—H(4)	0.94 (7)	N(7)—H(9)	0.99 (6)
N(3)—H(5)	0.63 (6)	N(7)—H(10)	0.80 (7)
C(2)—N(3)—H(4)	126 (4)	C(4)—N(7)—H(9)	120 (4)
C(2)—N(3)—H(5)	137 (6)	C(4)—N(7)—H(10)	113 (5)
H(4)—N(3)—H(5)	96 (7)	H(9)—N(7)—H(10)	126 (6)

of bis(oxamide oximato)cobalt(II)-oxamide oxime (Bekaroglu, Sarisaban, Koray & Ziegler, 1977), where the coordination of the Co atoms is tetragonal bipyramidal. In the Ni compound the amino substituents do not coordinate an adjacent metal, nor does the donating DMF molecule act as a ligand.

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Sodium Acetylphosphonate Acetic Acid Solvate

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Abstract. $\text{Na}^+\text{C}_2\text{H}_4\text{O}_4\text{P}^-\cdot\text{C}_2\text{H}_4\text{O}_2$, $M_r = 170.04$, monoclinic, $P2_1/c$, $a = 9.576$ (5), $b = 7.290$ (10), $c = 13.885$ (6) Å, $\beta = 120.87$ (2)°, $U = 832.0$ Å³, $Z = 4$, $D_x = 1.357$ g cm⁻³, $\mu(\text{Mo } K\alpha) = 3.2$ cm⁻¹. The structure was refined to $R = 0.038$ for 2288 unique reflexions. A network of non-bonded interactions links the different residues in the extended crystal structure.

Introduction. Acetylphosphonic acid, $\text{CH}_3\text{—CO—PO(OH)}_2$, is an analogue of pyruvic acid, and has been shown to be an effective reversible inhibitor of the enzyme complex pyruvate dehydrogenase (Harrison, Perham & Slater, unpublished; cited by Ambrose & Perham, 1976). An improved synthesis of acetylphosphonic acid (as its monosodium salt) has recently been designed (Dixon, Norris, Giddens & Sparkes, 1978) so that it might be better characterized and its

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properties checked. The final stage of the synthesis involved recrystallization from aqueous acetic acid/diethyl ether, the product forming as an acetic acid adduct. This acetic acid could not be removed, and the possibility that the adduct was covalent, *i.e.* that the —CO— group had become —C(OH)(OAc)— , could not be excluded. A crystallographic investigation was therefore undertaken to determine the nature of the adduct.

100 mg of the adduct were dissolved in a mixture of 0.2 ml water and 1.0 ml glacial acetic acid, and diethyl ether was layered onto the solution. Large colourless crystals, in the form of rectangular blocks, appeared after a few days. Since the adduct is somewhat hygroscopic, crystals were sealed in Lindemann tubes with the mother liquor. A crystal 1.0 × 0.4 × 0.4 mm, elongated along **b**, was used to collect data on a Syntex $P2_1$ diffractometer using Cu $K\alpha$ radiation and a graphite monochromator. 1401 reflexions were measured in the range $0 < 2\theta < 116^\circ$; after application

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of Lp corrections these gave 1140 unique reflexions with $F > 4\sigma(F)$. Systematic absences $0k0$, k odd, and $h0l$, l odd, indicated space group $P2_1/c$.

Automatic multisolution \sum_2 sign expansion using the program *SHELX* failed to give a solution because very few reflexions with high E values were present in parity groups *uug* or *ugu*. The program *XCSD* was therefore used; this incorporates a pseudotangent refinement to select all or part of the starting set (Roberts, Pettersen, Sheldrick, Isaacs & Kennard, 1973) and the negative quartet test NQUEST (De Titta, Edmonds, Langs & Hauptman, 1975). Six reflexions in parity groups *uug* and *ugu* were forced into the starting set. The best two E maps gave positions for all non-hydrogen atoms. However, the structure could not be successfully refined as several atoms possessed non-positive-definite thermal parameters. This could be attributed to the combined effects of absorption [$\mu(\text{Cu } K\alpha) = 33 \text{ cm}^{-1}$] and extinction.

A second data set was therefore collected, using the same crystal but with monochromated $\text{Mo } K\alpha$ radiation on a Stoe two-circle diffractometer. 3232 reflexions were collected for layers $h0l$ – $h8l$; averaging equivalent reflexions (Lp corrections being applied) gave 2288 unique data with $F > 4\sigma(F)$. Cell dimensions a , c and β were obtained by least-squares analysis of $h0l$ ω -angle measurements, and b from $0k0$ μ -angle measurements. Refinement, starting from atomic positions obtained from the first data set, proceeded to $R = 0.13$ (isotropic) and $R = 0.043$ (anisotropic). A

difference synthesis then gave positions for both acidic H atoms; the methyl H appeared to be disordered. In the final stages of refinement the acidic H refined freely; the methyl groups were successfully refined using a model of twofold disorder (Jones & Kennard, 1977). Chemically similar H atoms were assigned equal temperature factors. The final $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o|$ was 0.044, with a corresponding R of 0.038. The weighting scheme was $w = 1/[\sigma^2(F) + 0.001F^2]$. A final difference map showed no peaks $> 0.41 \text{ e } \text{Å}^{-3}$. Final atomic coordinates are given in Table 1, with derived bond lengths, angles and torsion angles in Tables 2–4.*

Discussion. The structure consists of Na^+ and $\text{CH}_3\text{—CO—P(O)(OH)(O}^-)$ ions and acetic acid molecules (Fig. 1); thus the adduct is not covalent. A complex

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33497 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atom coordinates ($\times 10^4$) and, for H, isotropic temperature factors ($\text{Å}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Na(1)	4363 (1)	4808 (1)	3615 (1)	
P(1)	4911 (1)	−106 (1)	3464 (1)	
O(1)	4833 (1)	1603 (1)	4042 (1)	
O(2)	4389 (1)	−1814 (1)	3887 (1)	
O(3)	4042 (1)	−72 (1)	2215 (1)	
C(1)	7102 (2)	−491 (2)	3974 (1)	
C(2)	8235 (2)	−828 (3)	5200 (1)	
O(4)	7573 (1)	−426 (2)	3309 (1)	
C(1')	1790 (2)	5715 (2)	4509 (1)	
O(1')	3045 (1)	5067 (1)	4641 (1)	
O(2')	1588 (1)	6161 (2)	5340 (1)	
C(2')	324 (2)	6046 (3)	3377 (1)	
H(1)	7410	−1140	5491	83 (5)
H(1a)	8034	65	5738	83 (5)
H(2)	9087	211	5732	83 (5)
H(2a)	9514	−848	5478	83 (5)
H(3)	8890	−2053	5230	83 (5)
H(3a)	7837	−2199	5236	83 (5)
H(4)	598	5849	2720	83 (5)
H(4a)	551	7156	2960	83 (5)
H(5)	−83	7436	3348	83 (5)
H(5a)	−669	6410	3496	83 (5)
H(6)	−622	5103	3257	83 (5)
H(6a)	12	4822	2869	83 (5)
H(10)	4729 (31)	−1821 (37)	4686 (23)	77 (5)
H(10')	2402 (36)	5635 (41)	5896 (23)	77 (5)

Table 2. Bond lengths (Å)

P(1)—O(1)	1.505 (3)	P(1)—O(2)	1.563 (3)
P(1)—O(3)	1.489 (2)	P(1)—C(1)	1.859 (3)
C(1)—C(2)	1.496 (3)	C(1)—O(4)	1.219 (3)
C(1')—O(1')	1.214 (3)	C(1')—O(2')	1.306 (3)
C(1')—C(2')	1.495 (3)	O(2)—H(10)	0.984 (32)
O(2')—H(10')	0.856 (25)		

Table 3. Bond angles (°)

O(1)—P(1)—O(2)	110.3 (2)
O(2)—P(1)—O(3)	110.8 (2)
O(2)—P(1)—C(1)	104.6 (2)
P(1)—C(1)—C(2)	118.4 (2)
C(2)—C(1)—O(4)	122.3 (2)
O(1')—C(1')—C(2')	123.0 (3)
P(1)—O(2)—H(10)	116.3 (17)
O(1)—P(1)—O(3)	117.1 (2)
O(1)—P(1)—C(1)	106.1 (2)
O(3)—P(1)—C(1)	107.1 (2)
P(1)—C(1)—O(4)	119.3 (2)
O(1')—C(1')—O(2')	123.2 (2)
O(2')—C(1')—C(2')	113.8 (2)
C(1')—O(2')—H(10')	101.9 (27)

Table 4. Torsion angles (°)

The sign convention is as defined by Klyne & Prelog (1960).

O(1)—P(1)—C(1)—C(2)	62.0 (2)
O(1)—P(1)—C(1)—O(4)	−116.7 (2)
O(2)—P(1)—C(1)—C(2)	−54.6 (2)
O(2)—P(1)—C(1)—O(4)	126.8 (2)
O(3)—P(1)—C(1)—C(2)	−172.2 (2)
O(3)—P(1)—C(1)—O(4)	9.1 (2)

network of non-bonded interactions links the different residues in the extended crystal structure (Table 5, Fig. 2); the Na⁺ ion achieves approximate octahedral coordination.

A search of the Cambridge Crystallographic Data Centre files (Kennard *et al.*, 1977) yielded several structures of phosphonates, but none of acyl phosphonates. Singly-ionized phosphonates show similar P—O bond lengths to the present compound, with one long P—OH and two short P—O bonds [e.g. 2-aminoethylphosphonic acid (Okaya, 1966): P—OH 1.569, other P—O 1.500, 1.513 Å]. The C—P bond lengths vary considerably (1.77–1.93 Å, the majority being <1.85 Å); the present compound thus displays a rather long

P—C bond (1.859 Å). There appears to be a correlation between P—C bond length and the substituents on the C atom, electronegative substituents giving longer P—C bonds [e.g. trisodium phosphonoformate: two O substituents, 1.972 Å (Naqvi, Wheatley & Foresti Serantoni, 1971); tetramethylformamidinium phosphonate: two N substituents, 1.890 Å (Daly, 1972); and trichlorophosphone: one O and one Cl₃C, 1.850 Å (Hohne & Lohs, 1969)].

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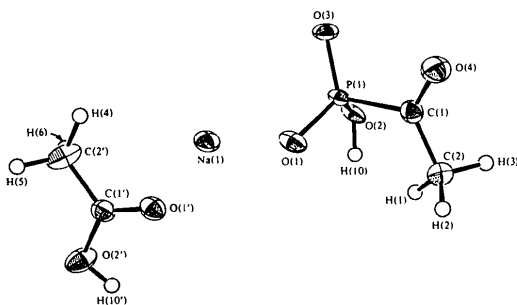


Fig. 1. ORTEP plot (Johnson, 1965) of the asymmetric unit, showing the atom-numbering scheme. Only one position of the disordered methyl groups is shown.

Table 5. Non-bonded distances

	Distance (Å)	Second atom at
Na(1)···O(1')	2.35	<i>x, y, z</i>
Na(1)···O(1)	2.40	<i>x, y, z</i>
Na(1)···O(2)	2.49	<i>x, 1 + y, z</i>
Na(1)···O(1')	2.42	$1 - x, 1 - y, 1 - z$
Na(1)···O(3)	2.34	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
Na(1)···O(4)	2.35	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
O(2)···O(1)	2.58	$1 - x, -y, 1 - z$
O(2')···O(3)	2.58	$x, \frac{1}{2} - y, \frac{1}{2} + z$

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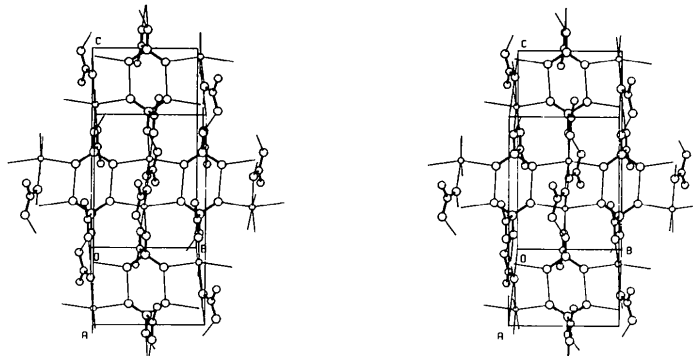


Fig. 2. Stereo packing diagram; non-bonded interactions are indicated by thin lines (H atoms omitted).