JOURNAL OF SOLID STATE CHEMISTRY 93, 88–95 (1991)

The 2-Methyl 4-Nitroanilinium Dihydrogenmonophosphate, $C_7H_9N_2O_2^+ \cdot H_2PO_4^-$, a Layer Structure Which Evidences the Structural Properties of $(H_2PO_4^-)_n$ Flexible Polyanion

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Received January 17, 1991

Chemical preparation and crystal structure of the 2-methyl 4-nitroanilinium dihydrogenmonophosphate are described. The cell constants are: $a = 32.16(5)$, $b = 8.230(6)$, $c = 8.056(6)$ Å, $z = 8$, space group *Pbca*. This layer structure is compared through its anionic network to various alkyl and aryl ammonium dihydrogenmonophosphates. A procedure for the crystal engineering of a new class of ferroic materials is suggested.

The $H_2PO_4^-$ anion is fascinating. Its ability to aggregate in flexible chains or layers in the presence of large inorganic or organic cations is now well supported by a great diversity of crystal structures containing it. The formation of the $(H_2PO_4^-)_n$ polyanion has been more and less emphasized by inorganic chemists interested in the hydrogen bond scheme (*1, 2*) and by organic chemists investigating biological materials or pharmacological drugs (*3–6*).

In a previous paper (*7*) a summary of the main organic salts containing $(H_2PO_4^-)_n$ polyanion was mentioned. A noteworthy property of $(H_2PO_4^-)_n$ chains or layers is the reflection in its framework of the chirality of the associated organic cations. The formation of organic chiral salts is easy when the chiral cations are associated with little and spherical monovalent anions, but if the ratio charge/volume of the associated counter anion is modified (for example with the use of a $P_6O_{18}^{-6}$ cyclic or a $P_4O_{13}^{-6}$ tetraphosphate anion) with a purpose of crystal engineering then it is difficult to crystallize such salts without solvent interference. More often amorphous materials are produced or starting reagents are regenerated. Few examples illustrate the effect of the chiral organic cations on the $H_2PO_4^-$ aggregation:

—$(H_2PO_4^-)_n$ chains with 2_1 symmetry occur as counter anion in (+)amphetamine dihydrogen monophosphate (*5*), L-β-methyl alaninium dihydrogenmonophosphate (7) and L-α-alaninium dihydrogenmonophosphate (8).

—$(H_2PO_4^-)_n$ layers with C2 symmetry are described in (−)ephedrine dihydrogen monophosphate (3).

The MNA (2-methyl 4-nitroaniline) is a well known nonlinear optical organic material (*9, 10*). Our aim was to build up a layer structure using $(H_2PO_4^-)_n$ polyanions in which the MNA^+ (2-methyl 4-nitroanilinium) cations would be sandwiched. The for-

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mation of MNA^+ destroys the intramolecular charge transfer and consequently the nonlinear optical properties. The anchoring mechanism of MNA^+ on the $(H_2PO_4^-)_n$ polyanion and the possibility of obtaining an acentric crystal were the main motivations which led us to prepare this salt. It is also an intermediate step in the polar crystal engineering using aryl derivatives like cations and $(H_2PO_4^-)_n$ like counter anions. The first step was the crystallization of substances like the 2-carboxyanilinium dihydrogenmonoarsenate (monophosphate) (*11*). The third step was to choose an appropriate nitroaniline derivative which may be anchored on the phosphate layer without loss of the intramolecular charge transfer or with a weak attenuation of it: the result was the production of the acentric phase, the 2-amino 5-nitropyridinium dihydrogenmonophosphate (*Pna*2_1) (*12*).

Chemistry

The MNA, insoluble in water, may be dissolved in concentrated monophosphoric acidic aqueous solutions. Concentrated acid (8 cm^3; 85% H_3PO_4, $d = 1.7$, Prolabo Rectapur) are filled in a test tube kept at 60°C in an oil bath. The MNA ($C_7H_8N_2O_2$, Sigma Chemical Co.) is added gradually in the viscous acidic solution. The test tube is pulled out of the oil bath and cooled at room temperature. If the precipitation of little crystals does not occur the test tube is again maintained at 60°C and MNA added. This process is repeated until the first crystals appear. The brown viscous solution is removed to a crystallizer and large platelets are formed after several days. The observed crystals are white and of very small thickness, unfitted for an X-ray structural determination. They are dried and dissolved in methyl acetate. The slow evaporation of such a solution provides large platelets of 7 × 3 mm area and 1 mm thickness. The chemical formula, $C_7H_9N_2O_2^+ \cdot H_2PO_4^-$, has been established on the basis of the X-ray crystal structure investigations. Crystals are instantaneously decomposed in water and MNA regenerated.

The previous chemical reactions could be written

$$\underset{\text{(yellow crystals)}}{C_7H_8N_2O_2 + H_3PO_4} \rightarrow \underset{\text{(white crystals)}}{C_7H_9N_2O_2^+ \cdot H_2PO_4^-} \quad (1)$$

$$C_7H_9N_2O_2^+ \cdot H_2PO_4^- + H_2O \rightarrow C_7H_8N_2O_2 + H_3O^+ + H_2PO_4^- \quad (2)$$

Reaction (2) shows that the basicity of water is stronger than that of MNA and gives light on the preparation method. The restitution of H_3PO_4 following (2) is complete. The H_3PO_4 solution is strongly colored by the small quantity of the remaining MNA (<0.01%).

Crystal Structure Investigation

The crystal used for data collection was a platelet: 1.6 × 1.12 × 0.32 mm^3. It was placed in a glass capillary containing a small amount of mother solution. Twenty-five re-

TABLE I

CRYSTAL DATA AND PARAMETERS USED FOR THE X-RAY DATA COLLECTION

Cell constants: $a = 32.16(5)$, $b = 8.230(6)$, $c = 8.056(6)$ Å
Space group: *Pbca*
Formula units: 8
Calculated density, $d_x = 1.559$ g/cm^3
MW = 250.1, $F(000) = 1040$
Absorption coefficient ($\lambda\kappa\bar{\alpha}$Mo): 2.824 cm^{-1}
Apparatus: Nicolet XRD
Wavelength, $\lambda\kappa\bar{\alpha}$Mo, 0.71073 Å
Monochromator: graphite plate
ω scan, θ range: 1.5–40°, scan width: 1.4°, scan speed: 1 to 3°/min
Total background measuring time: 20% of τ ($0.47 \leq \tau \leq 1.4$ min)
Number of collected reflections with $I \geq 2\sigma(I)$: 2285
$H_{max} = 59$, $K_{max} = L_{max} = 15$
Reference reflections: 713, 434, $42\bar{2}$ (no significant variation)

TABLE II

FINAL ATOMIC COORDINATES, B_{eq} FOR NONHYDROGEN ATOMS AND B_{iso} FOR HYDROGEN ATOMS

$$B_{eq} = \frac{4}{3}\sum_i \sum_j \beta_{ij}\, a_i a_j$$

	X	Y	Z	B_{eq}, B_{iso}(Å^2)
P	0.03185(1)	0.03163(5)	0.73844(5)	1.993(6)
O1	0.02875(6)	−0.1079(2)	0.8683(2)	3.42(3)
O2	0.05376(5)	−0.0405(2)	0.5829(2)	3.81(3)
O3	−0.01090(4)	0.0899(2)	0.6905(2)	2.32(2)
O4	0.05909(4)	0.1567(2)	0.8166(2)	2.81(2)
O5	0.24007(6)	0.7539(3)	0.9104(3)	5.93(5)
O6	0.26667(6)	0.5826(3)	0.7408(3)	5.59(5)
C1	0.11834(5)	0.4894(2)	0.6792(2)	2.26(3)
C2	0.15227(6)	0.3996(3)	0.6208(2)	2.53(3)
C3	0.19148(6)	0.4579(3)	0.6615(3)	2.97(4)
C4	0.19532(6)	0.5972(3)	0.7541(3)	3.15(4)
C5	0.16169(7)	0.6868(3)	0.8045(4)	3.81(4)
C6	0.12248(7)	0.6330(3)	0.7618(3)	3.41(4)
C7	0.14760(7)	0.2581(3)	0.0304(4)	4.44(5)
N1	0.07705(5)	0.4281(2)	0.6403(2)	2.21(3)
N2	0.23704(6)	0.6488(3)	0.8051(3)	4.14(4)
H(O1)	0.0222(9)	0.826(3)	0.833(4)	4.9(7)
H(O2)	0.0389(8)	0.956(3)	0.506(3)	4.4(6)
H1	0.0737(7)	0.402(3)	0.532(3)	2.4(4)
H2	0.0708(8)	0.338(3)	0.696(3)	3.9(6)
H3	0.0573(7)	0.494(3)	0.672(3)	2.5(4)
H4	0.173(1)	0.292(4)	−0.008(4)	5.6(8)
H5	0.132(1)	0.254(5)	0.938(5)	8(1)
H6	0.125(1)	0.319(4)	0.077(5)	6.9(9)
H7	0.2142(8)	0.400(3)	0.628(3)	4.0(6)
H8	0.167(1)	0.771(4)	0.875(4)	6.4(8)
H9	0.0985(8)	0.699(3)	0.791(3)	2.7(5)

flection positions were collected (9° $< \theta <$ 15°) on a Nicolet XRD diffractometer ($\lambda K\bar{\alpha}$Mo). They were used for the refinement of the cell constants. The space group *Pbca* was determined using the entire set of collected reflections. Relevant experimental parameters for data collection are described in Table I. Intensity data were processed in the usual way: L.P. correction, no extinction correction, no absorption correction. The structure was solved by direct methods (*13*) and successive Fourier synthesis (Table II). H atoms were located from difference Fourier maps. Full matrix least-squares refinements using anisotropic thermal parameters for P, O, N, C atoms and isotropic thermal factors for H atoms converged at $R = 0.045$ for 2285 reflections, $I > 2\sigma(I)$. A unitary weighting scheme was chosen because only strong and medium reflections have been used: 3441 nonzero unique reflections collected originally and 1156 rejected due to the crystal size with respect to the X-ray beam dimension. The maximum peak in the last Fourier map is equal to 0.35e/Å^3. Enraf-Nonius (1977) SDP was used for all calculations (*14*). Computer used was a Microvax II.

Discussion

The $C_7H_9N_2O_2^+ \cdot H_2PO_4^-$ is a layer structure in which the MNA^+ cations are sandwiched between $H_2PO_4^-$ sheets (Fig. 1). The inorganic moiety is a network of PO_4 tetrahedra connected by short hydrogen bonds (Fig. 2). The MNA^+ cations are anchored on the anionic subnetwork by three hydrogen bonds (Fig. 3). O3 is one time an H acceptor and O4 is two times from two distinct MNA^+ cations. The main feature of the alkyl or aryl ammonium dihydrogenmonophosphates is that the anionic subnetwork is built up through short hydrogen bonds and the organic cations are bound to the phosphate layers by larger ones. When cations possess two functional groups, one an H donor, the other an H acceptor, large hydrogen bonds occur between them. The role of the organic cations is to organize the anionic aggregates in layers or chains of various typical geometries following the position and the number of functional groups which are hydrogen donors and acceptors. Figure 2 and Fig. 4 show two close $(H_2PO_4^-)_n$ subnetworks: in 2-methyl 4-nitroanilinium dihydrogenmonophosphate three hydrogen atoms are accepted by one $H_2PO_4^-$ and in 2-carboxyanilinium dihydrogenmonoarsenate (*11*) the ratio is $4H/1H_2AsO_4^-$. The situation is quite different in α-methyl alaninium dihydrogenmonophosphate (*7*) (Fig. 5). Each $H_2PO_4^-$ unit shares an H atom statistically

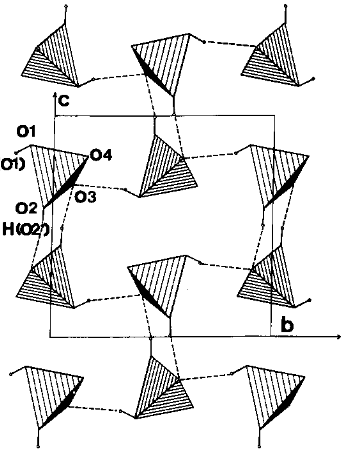

FIG. 2. Periodic arrangement of $(H_2PO_4^-)_n$ layer in the (*b*, *c*) projection.

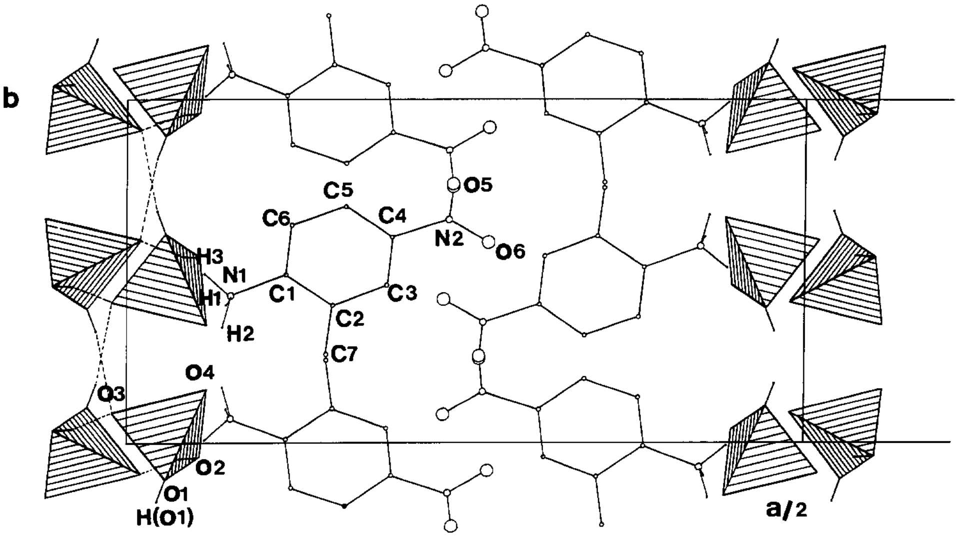

FIG. 1. A partial (*a*, *b*) projection of $C_7H_9N_2O_2^+ \cdot H_2PO_4^-$.

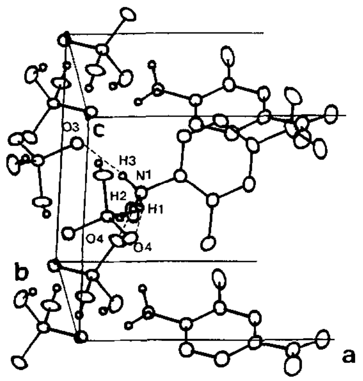

FIG. 3. A detailed representation of the anchorage of the MNA^+ cation on the $(H_2PO_4^-)_n$ layer (Ortep Program (*24*)).

with its neighbor. The same network has been found by Adams (*4*) in aminoguanidinium dihydrogenmonophosphate and recently in the cytosinium dihydrogen monophosphate (*16*). In these structures each $H_2PO_4^-$ accepts three hydrogen atoms and the donor groups are situated in opposition. A last type of $(H_2PO_4^-)_n$ layer has been observed in the glycine monophosphate (*17*) (Fig. 6): the anionic network is the acceptor of three H atoms from the organic cation/$1H_2PO_4^-$. The main geometrical features of the MNA^+ cation are noted in Table III.

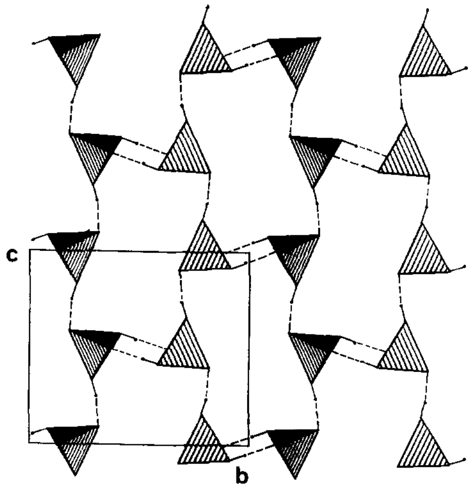

FIG. 4. (*b*, *c*) projection of $(H_2AsO_4^-)_n$ subnetwork in the structure of 2-carboxyanilinium dihydrogenmonoarsenate $C_7H_8NO_2^+ \cdot H_2AsO_4^-$.

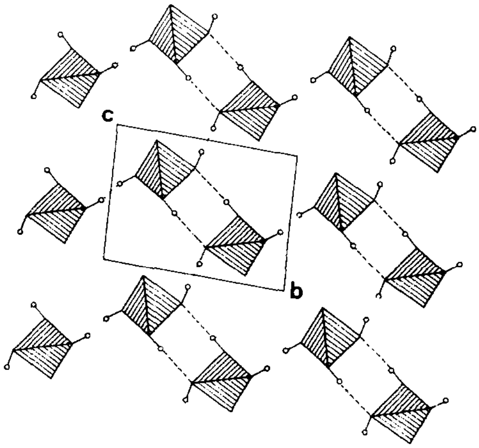

FIG. 5. (*b*, *c*) projection of $(H_2PO_4^-)_n$ subnetwork in the structure of the α-methyl alaninium dihydrogenmonophosphate $C_4H_{10}N_3O_2^+ \cdot H_2PO_4^-$.

Conclusion

Only $(H_2PO_4^-)_n$ centric layers have been described previously and few acentric ones have been mentioned until now. Centric or

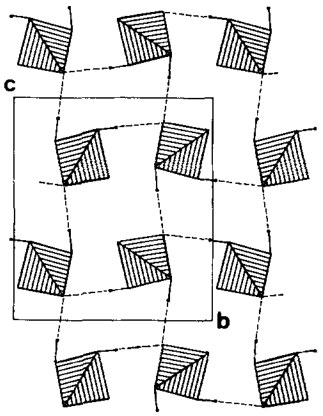

FIG. 6. (*b*, *c*) projection of $(H_2PO_4^-)_n$ layer in the structure of the glycine monophosphate $C_2H_6NO_2^+ \cdot H_2PO_4^-$.

TABLE III

Main Interatomic Distances (Å) and Bond Angles (°) and Their e.s.d.

The PO_4 tetrahedron in $(H_2PO_4^-)_n$

P	O1	O2	O3	O4
O1	1.557(1)	2.498(2)	2.515(2)	2.422(2)
O2	106.8(1)	1.555(1)	2.495(2)	2.491(2)
O3	110.4(1)	109.2(1)	1.506(1)	2.529(2)
O4	105.2(1)	109.7(1)	115.1(1)	1.491(1)

P–O1–H(O1) = 110(3)
P–O2–H(O2) = 112(2)

The 2-methyl 4-nitroanilinium cation

N1–C1	1.444(2)	C4–C5	1.370(3)	C7–H6	0.96(3)
C1–C2	1.383(3)	C5–C6	1.380(3)	C3–H7	0.91(2)
C2–C7	1.495(3)	C6–C1	1.388(3)	C5–H8	0.91(3)
C2–C3	1.388(3)	N1–H1	0.90(2)	C6–H9	0.97(2)
C3–C4	1.374(3)	N1–H2	0.89(3)		
C4–N2	1.465(3)	N1–H3	0.85(2)		
N2–O5	1.215(3)	C7–H5	0.89(4)		
N2–O6	1.213(3)	C7–H4	0.93(3)		

C2–C1–C6	122.4(2)	C5–C6–H9	119(1)		
C2–C1–N1	118.9(2)	C1–C6–H9	122(1)		
C6–C1–N1	118.6(2)	C1–C6–C5	119.3(2)		
C1–C2–C3	117.4(2)	C2–C7–H4	109(2)	O5–N2–O6	123.6(2)
C1–C2–C7	122.1(2)	C2–C7–H5	115(2)	O5–N2–C4	118.4(2)
C3–C2–C7	120.4(2)	C2–C7–H6	110(2)	O6–N2–C4	118.0(2)
C2–C3–C4	119.9(2)	H4–C7–H5	103(3)		
C2–C3–H7	119(2)	H4–C7–H6	131(3)		
C4–C3–H7	121(2)	H5–C7–H6	85(3)		
C3–C4–C5	122.6(2)	C1–N1–H1	112(1)		
C3–C4–N2	118.5(2)	C1–N1–H2	114(2)		
C5–C4–N2	118.9(2)	C1–N1–H3	114(2)		
C4–C5–C6	118.3(2)	H1–N1–H2	105(2)		
C4–C5–H8	116(2)	H1–N1–H3	110(2)		
C6–C5–H8	125(2)	H2–N1–H3	101(2)		

Hydrogen bonds

	O(N)–H	H---O	O(N)---O	O(N)–H---O
O1–H(O1)---O3	0.64(3)	1.99(3)	2.596(2)	157(3)
O2–H(O2)---O3	0.78(3)	1.86(3)	2.630(2)	167(3)
N1–H1---O4	0.90(2)	1.86(2)	2.760(2)	172(2)
N1–H2---O4	0.89(2)	1.81(2)	2.710(2)	178(2)
N1–H3---O3	0.87(2)	2.02(2)	2.856(2)	160(2)

TABLE III—*Continued*

Equation of least-squares plane of benzene ring and shifts of atoms from it (Å)

$1.10(3)x + 4.343(7)y - 6.837(4)z = -2.336(8)$ based on crystallographic axes.
Atoms used for the research of least-squares plane equation:
C1, −0.009(2); C2, −0.004(2); C3, 0.013(2),
C4, −0.010(2); C5, −0.003(3); C6, 0.012(2).
Atoms of functional groups:
O5, −0.349(2); O6, 0.096(2); N1, −0.096(2),
N2, −0.089(2); C7, −0.079(3).

acentric chains are another possible aggregation of $H_2PO_4^-$ units (*7*). The anisotropic character brought to the structures built up with the $(H_2PO_4^-)_n$ polyanion and the dipole moment associated with each $H_2PO_4^-$ unit evidence its use in the crystal engineering of piezoelectric or polar materials. This approach has been illustrated by the 2-amino 5-nitropyridinium dihydrogenmonophosphate (*12*). Many organic molecules bearing dipole moments or having an intramolecular charge transfer character may be sandwiched between $(H_2PO_4^-)_n$ layers or chains through the hydrogen bonds inherent to functional groups.

The $(H_2PO_4^-)_n$ polyanion may also aggregate water or monophosphoric acid molecules to form original frameworks like in glycylglycine phosphate monohydrate (*18*); 4-amino-pyridinium dihydrogenmonophosphate monohydrate (*19*); L-histidinium dihydrogenmonophosphate monophosphoric acid, $C_6H_{10}N_3O_2^+ \cdot H_2PO_4^- \cdot H_3PO_4$ (*20*); ethylenediammonium dihydrogentetraoxophosphate pentahydrogen bis (tetraoxophosphate), $C_2H_{10}N_2^{2+} \cdot H_2PO_4^- \cdot H_5P_2O_8^-$ (*21*); and pyridinium dihydrogenmonophosphate monophosphoric acid, $C_5H_6N^+ \cdot H_2PO_4^- \cdot H_3PO_4$ (*22*).

This ability of the $H_2PO_4^-$ anion and the H_3PO_4 molecule to aggregate between them, the surprising structure of 2DL-alanine monophosphoric acid (*23*) $(NH_3^+{-}CH(CH_3){-}COO^-)_2 \cdot H_3PO_4$ in which the DL-alaninium zwitterions are sandwiched between chains of monophosphoric acid, and the possible formation of addition compounds like $CH_3COOH \cdot H_3PO_4$ (*25*) in which independent layers of H_3PO_4 have been evidenced strongly suggest the possible development of an H_3PO_4-like clathrate chemistry.

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