

Pour le système $[M^{2+} \cdot Br(1)^-] \cdot Br(2)^-$, l'atome $Br(2)^-$ ($\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$) pris pour le calcul est le plus proche du complexe $[M^{2+} \cdot Br(1)^-]$; le fait marquant est que l'HOMO correspond maintenant aux trois OM construites à partir des trois OA, p_x, p_y et p_z de $Br(2)^-$, ne montrant aucun couplage avec la molécule M^{2+} . Il interagit faiblement avec le cycle pyridinium m_1 de la molécule située en $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$.

La conformation de la molécule étudiée, dans le cristal, est fortement influencée par la présence des ions I^- dont l'un est littéralement complexé. La cohésion cristalline réside d'une part, dans les interactions de type ionique entre les ions I^- et les noyaux pyridinium et d'autre part, de liaisons hydrogène mettant en jeu les fonctions $C-CH=N-OH$.

Nous envisageons l'étude du dérivé dichloré; l'ion chlore Cl^- nettement moins volumineux que l'ion I^- devrait avoir moins tendance à être encagé par la molécule. Nous n'avons malheureusement pu

obtenir, à ce jour, un cristal satisfaisant de ce composé.

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Structure of Dimethylethanolammonium Dihydrogenmonophosphate Monohydrate

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Abstract. 1-Hydroxy-2-methyl-2-propylammonium dihydrogenphosphate monohydrate, $C_4H_{12}NO^+ \cdot H_2PO_4^- \cdot H_2O$, $M_r = 205.15$, monoclinic, $P2_1/n$, $a = 16.542$ (3), $b = 9.170$ (2), $c = 6.192$ (3) Å, $\beta = 92.63$ (5)°, $V = 938.3$ (9) Å³, $Z = 4$, $D_x = 1.452$ Mg m⁻³, $\lambda(\text{Ag } K\alpha) = 0.5608$ Å, $\mu = 0.161$ mm⁻¹, $F(000) = 440$, $T = 295$ K, final $R = 0.034$ for 2123 unique reflections. Wide ribbons of $C_4H_{12}NO^+$ groups and water molecules, and $H_2PO_4^-$ infinite chains parallel to **b** alternate along the **c** direction. The cohesion between the different groups is maintained by a three-dimensional network of hydrogen bonds.

Introduction. The present work is part of a systematic investigation of the interaction of various phosphoric acids with amines, amino acids and amino alcohols.

In the field of amino-alcohol phosphates only two compounds have been described up to now: the first was ethanolammonium monophosphate studied by Isabev, Ibragimov, Talipov, Saibova & Aripov (1981), the second was the cyclo-tetraphosphate of the same amino alcohol (Averbuch-Pouchot, Durif &

Guitel, 1988). The title compound is the first example of a phosphate of dimethylethanolammonium.

Experimental. Single crystals were prepared by slow evaporation, at room temperature, of an aqueous solution of β -aminoisobutylalcohol, $(CH_3)_2C(NH_2) \cdot CH_2OH$, and phosphoric acid, H_3PO_4 , in a stoichiometric ratio. After several days, colourless monoclinic prisms appeared.

Prism fragment: $0.48 \times 0.38 \times 0.24$ mm. Density not measured. Enraf-Nonius CAD-4 diffractometer, graphite monochromator. Systematic absences: $0k0$, $k = 2n$; $h0l$, $h + l = 2n$. 24 reflections ($10 < \theta < 13^\circ$) for refining unit-cell dimensions. $\omega/2\theta$ scan. 3152 non-zero unique reflections collected ($3 < \theta < 35^\circ$). $R_{int} = 0.015$. $\pm h, k, l$, $h_{max} = 28$, $k_{max} = 16$, $l_{max} = 10$. Scan width = 1.30° , scan speed = $0.022^\circ \text{ s}^{-1}$, total background measuring time 30 s. Two orientation ($\bar{9}30$ and $\bar{9}\bar{3}0$) and one intensity ($5\bar{5}\bar{1}$) reference reflections (no significant variation).

Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods with *MULTAN77* (Main, Lessinger, Woolfson,

Germain & Declercq, 1977). H atoms from difference Fourier map. Anisotropic full-matrix least-squares refinement (on F), isotropic for H atoms. Function minimized $\sum w(|F_o| - |F_c|)^2$. Unit weights. Final refinement cycles with 2123 reflections corresponding to $I > 4\sigma(I)$. Final $R = 0.034$ ($wR = 0.036$). $S = 0.576$. Max. $\Delta/\sigma = 0.02$ for y of H(2). Max. peak height in the final difference Fourier synthesis $0.372 \text{ e } \text{\AA}^{-3}$. Final R value is 0.064 for the complete set of 3152 independent reflections. No extinction correction. Scattering factors for neutral atoms and f' , f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV). Enraf-Nonius (1977) *SDP* employed for all calculations. Computer used: MicroVAX 2.

Discussion. Table 1* reports the final atomic coordinates while Fig. 1 represents a projection of the atomic arrangement down c and Fig. 2 gives details of the hydrogen-bond network down the same axis.

The structure can be described as chains of H_2PO_4^- groups running along the 2_1 axes at $\frac{1}{4}$, 0 , $\frac{1}{4}$ and $\frac{3}{4}$, 0 , $\frac{3}{4}$, each chain being inserted between ribbons (width $a/2 = 8.27 \text{ \AA}$) of $\text{C}_4\text{H}_{12}\text{NO}^+$ units and water molecules at $z = \frac{3}{4}$ for the former chain and $z = \frac{1}{4}$ for the latter.

The shortest P—P distance in the chain is $4.7195(7) \text{ \AA}$. The H_2PO_4^- ions are linked by hydrogen bonds along the 2_1 axis *via* the H(2) atom (Fig. 1). They are connected to the organic groups of the adjacent cells along the c direction by means of the H(3) atom. Moreover, the O atoms O(1) and O(4) of the phosphate anion accept hydrogen bonds from the water molecule (Fig. 2).

Table 2 reports the main interatomic distances and bond angles in all these groups. As usual, the P—OH distances [P—O(2) 1.557 and P—O(3) 1.566 \AA] are significantly longer than the other P—O distances (1.493 and 1.502 \AA).

As also shown in Table 2, the $\text{C}_4\text{H}_{12}\text{NO}^+$ entity has a tetrahedral geometry with C(2) in the centre and C(1), C(3), C(4) and N at the apices of the polyhedron.

The amino group is protonated by a phosphate H atom. N and O atoms act as hydrogen-bond donors. Two bifurcated hydrogen bonds link N to the O atoms of the phosphate group and of the organic group itself. This type of configuration has already been observed in phosphoric compounds with organic groups: for example in the crystal structure

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and main interatomic distances and bond angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53082 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates and B_{eq} 's with e.s.d.'s in parentheses

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{\text{eq}} (\text{\AA}^2)$
P	0.28340 (3)	0.34908 (5)	0.26869 (7)	1.825 (6)
O(1)	0.29398 (9)	0.3223 (2)	0.5061 (2)	2.53 (2)
O(2)	0.21306 (9)	0.4573 (2)	0.2120 (2)	2.82 (3)
O(3)	0.36285 (9)	0.4250 (2)	0.1988 (2)	2.80 (3)
O(4)	0.23522 (9)	0.7167 (1)	0.3675 (2)	2.56 (2)
O	0.8572 (1)	-0.0130 (2)	0.2933 (2)	3.01 (3)
O(W)	0.8584 (1)	0.3906 (2)	0.2880 (3)	3.65 (3)
N	0.6577 (1)	0.1888 (2)	0.2748 (3)	2.41 (3)
C(1)	-1.0163 (1)	0.6731 (3)	0.1338 (4)	3.40 (4)
C(2)	0.9240 (1)	0.7550 (2)	0.2673 (3)	2.05 (3)
C(3)	0.5797 (1)	0.4115 (2)	0.3068 (3)	2.48 (3)
C(4)	0.0550 (1)	0.2584 (3)	0.4936 (3)	3.05 (4)

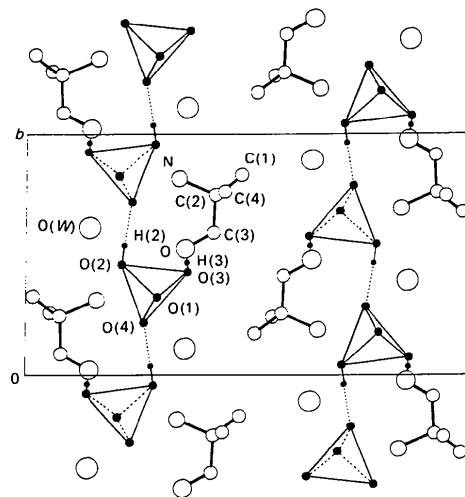


Fig. 1. Projection of the atomic arrangement of $\text{C}_4\text{H}_{12}\text{NO}^+\cdot\text{H}_2\text{PO}_4\cdot\text{H}_2\text{O}$ down c . Only H atoms of the phosphoric anions are represented.

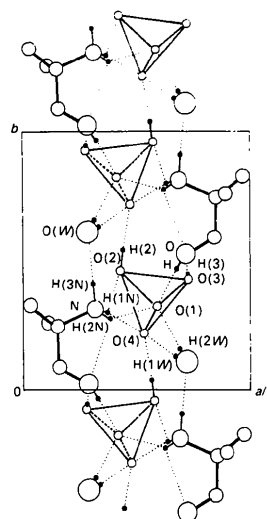


Fig. 2. Scheme of the hydrogen bonding between $x = 0$ and 0.5 . Only H atoms implicated in the hydrogen bonds (dotted lines) are shown.

Table 2. Main interatomic bond distances (Å) and angles (°) with e.s.d.'s in parentheses

PO ₄ tetrahedron				
P	O(1)	O(2)	O(3)	O(4)
O(1)	1.493 (1)	112.3 (1)	106.5 (1)	115.6 (1)
O(2)	2.534 (2)	1.557 (2)	106.4 (1)	104.9 (1)
O(3)	2.450 (2)	2.501 (2)	1.566 (2)	110.9 (1)
O(4)	2.534 (2)	2.425 (2)	2.527 (2)	1.502 (1)
P—P		4.7195 (7)		
C ₄ H ₁₂ NO tetrahedral group				
C(2)	C(1)	C(3)	C(4)	N
C(1)	1.515 (3)	108.9 (2)	111.6 (2)	108.0 (2)
C(3)	2.459 (3)	1.508 (3)	112.3 (2)	108.1 (2)
C(4)	2.502 (3)	2.507 (3)	1.510 (3)	107.7 (2)
N	2.435 (3)	2.429 (3)	2.425 (3)	1.494 (2)
C(3)—O	1.419 (3)	C(2)—C(3)—O		110.6 (2)
Hydrogen bonds				
O(N)—H...O	O(N)—H	H...O	O(N)—H—O	O(N)—O
O(2)—H(2)...O(4)	0.81 (3)	1.78 (3)	175 (3)	2.586 (2)
O(3)—H(3)...O	0.65 (2)	1.98 (2)	177 (3)	2.635 (2)
O—H...O(1)	0.75 (2)	1.93 (2)	173 (2)	2.673 (2)
O(W)—H(1W)...O(4)	0.76 (2)	2.12 (2)	172 (3)	2.868 (2)
O(W)—H(2W)...O(1)	0.74 (2)	2.07 (2)	167 (2)	2.797 (2)
N—H(1N)...O(4)	0.85 (2)		162 (2)	2.905 (2)
N—H(1N)...O(2)	2.53 (2)		127 (2)	3.120 (2)
N—H(2N)...O(1)	2.08 (3)		142 (2)	2.865 (2)
0.92 (3)				
N—H(2N)...O	2.53 (3)		121 (1)	2.776 (2)
N—H(3N)...O(W)	0.89 (3)	1.89 (3)	176 (2)	2.773 (2)
H(1W)—O(W)—H(2W)		105 (3)		

of tris(ethylenediammonium) bis(cyclo-triphosphate), [NH₃(CH₂)₂NH₃]₃(P₃O₉)₂ (Averbuch-Pouchot, Durif & Guitel, 1989). One quasi-linear hydrogen bond joins N to the water molecule, another one joins O to the PO₄ tetrahedron.

So the succession of C₄H₁₂NO⁺ and O(W) ribbons and H₂PO₄⁻ chains is stabilized by a three-dimensional network of hydrogen bonds and geometrical details of this hydrogen-bond scheme are listed in Table 2. Some characteristic features should be noted: there is no direct bonding between the different organic groups in a ribbon and no bonding at all between the ribbons or chains related by centrosymmetry.

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Structure of *N*-(3,6-Dimethoxy-17-methyl-4,5-epoxy-6,14 α -etheno-7 α -isomorphinanylcarbonyl)-*L*-phenylalanine Ethyl Ester Hydrochloride

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Abstract. C₃₃H₃₉N₂O₆⁺.Cl⁻, *M_r* = 595.13, orthorhombic, *P*2₁2₁2₁, *a* = 10.678 (1), *b* = 11.365 (1), *c* = 24.664 (2) Å, *V* = 2993.1 (5) Å³, *Z* = 4, *D_x* = 1.321 g cm⁻³, λ (Mo *K* α) = 0.71073 Å, μ = 1.7 cm⁻¹, *F*(000) = 1264, *T* = 295 K, *R* = 0.052 for 2450 observed reflections with *I* > 2.5 σ (*I*). The phenylalanine residue is found to have no significant effect on the geometry of the ethenoisomorphinan skeleton. The amide H is intramolecularly hydrogen

bonded to the carbonyl O of the peptide moiety and not to the methoxy ether O. This results in an orientation of the peptide side chain more or less parallel to the piperidine moiety.

Introduction. The interaction of opioids with the opioid receptor has still not been clarified, in spite of several valuable receptor models (Kolb, 1987; and references cited therein). Conformational analysis in