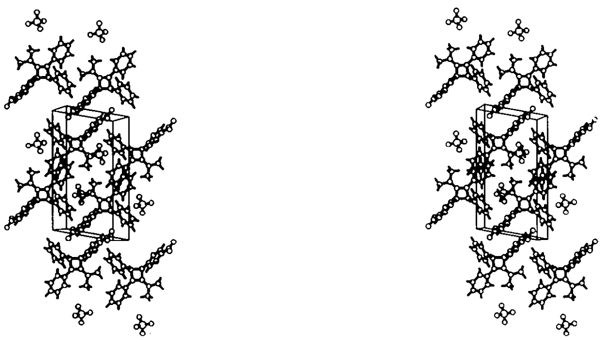

Fig. 3. Stereo drawing of the unit-cell contents, viewed approximately perpendicular to the *bc* plane.

O(38) (at $1+x, y, z$), 3·770 (6) Å respectively. The perchlorate anions are accommodated between these rows in proximity to N(21) with a closest approach, N(21) to O(2) (at $1-x, 1-y, 1-z$), of 3·559 (8) Å. However, none of the intermolecular distances is significantly shorter than the sum of the corresponding van der Waals radii.

The SERC is thanked for financial support (research studentship to ARW).

References

De Poortere, M., Marchand-Brynaert, J. & Ghosez, L. (1974). *Angew. Chem. Int. Ed. Engl.* **13**, 267–268.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Pauling, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sternhell, S. (1969). *Q. Rev. Chem. Soc.* **23**, 236–270.

Acta Cryst. (1988). C**44**, 888–890

Structure of Glycine *cyclo*-Tetraphosphate

By M. T. Averbuch-Pouchot, A. Durif and J. C. Guitel

Laboratoire de Cristallographie associé à l'Université Scientifique Technologique et Mèdicale de Grenoble, Centre National de la Recherche Scientifique, 166X, 38042 Grenoble CEDEX, France

(*Received* 2 *September* 1987; *accepted* 12 *January* 1988)

Abstract. $(NH_3CH_2COOH)_4P_4O_{12}$, $4C_2H_6NO_2^+.P_4O_{12}^{4-}$, $M_r = 620{\cdot}18$, triclinic, $P\bar{1}$, $a = 7{\cdot}988\ (5)$, $b = 8{\cdot}449\ (5)$, $c = 9{\cdot}739\ (5)$ Å, $\alpha = 111{\cdot}64\ (5)$, $\beta = 105{\cdot}27\ (5)$, $\gamma = 99{\cdot}40\ (5)°$, $V = 564\ (2)$ Å^3, $Z = 1$, $D_x = 1{\cdot}826$ Mg m^{-3}, $\lambda(\mathrm{Ag}\ K\alpha) = 0{\cdot}5608$ Å, $\mu = 0{\cdot}239$ mm^{-1}, $F(000) = 320$, $T = 295$ K, final $R = 0{\cdot}025$ for 3393 unique reflexions. The title compound is the first example of an amino acid *cyclo*-tetraphosphate. In its atomic arrangement the non-acidic cyclic phosphoric group $(P_4O_{12})^{4-}$ is interconnected by hydrogen bonds to eight different $(C_2H_6NO_2)^+$ groups. A complete hydrogen-bond scheme is reported.

Introduction. As part of a systematic investigation of amino acid phosphates we previously reported chemical preparations and crystal structures of glycine monophosphate and glycine *cyclo*-triphosphate (Averbuch-Pouchot, Durif & Guitel, 1988). In the present work we describe the first amino acid *cyclo*-tetraphosphate: $(gly)_4.P_4O_{12}$.

Experimental. Crystals of glycine *cyclo*-tetraphosphate were prepared by a metathesis reaction deriving from that described by Boullé (1941) for the preparation of water-soluble inorganic *cyclo*-triphosphates: the silver *cyclo*-triphosphate monohydrate being replaced by the silver *cyclo*-tetraphosphate $Ag_4P_4O_{12}$. To a slurry in water of the sparingly soluble silver *cyclo*-tetraphosphate is slowly added an aqueous solution of glycine hydrochloride in stoichiometric ratio 1:4. The reaction is

$$Ag_4P_4O_{12} + 4(NH_3CH_2COOH)Cl \rightarrow 4AgCl + (NH_3CH_2COOH)_4P_4O_{12}.$$

After about two hours of mechanical stirring the insoluble silver chloride is eliminated by filtration. The resulting aqueous solution is then kept at room temperature. After some days of evaporation, colorless flat prisms of glycine *cyclo*-tetraphosphate appear in the solution. Crystal size: 0·29 × 0·35 × 0·24 mm. Density not measured. Philips PW1100 diffractometer, graphite

0108-2701/88/050888-03$03.00

Table 1. *Atomic coordinates and* B_{eq}(Å^2) *for glycine cyclo-tetraphosphate*

E.s.d.'s are given in parentheses.

$$B_{eq} = \tfrac{4}{3}\sum_i \sum_j \mathbf{a}_i.\mathbf{a}_j \beta_{ij}.$$

	x	y	z	B_{eq}
P(1)	0·21214 (4)	0·06333 (4)	0·22473 (3)	1·175 (5)
P(2)	0·13897 (4)	0·20515 (4)	0·98273 (3)	1·203 (5)
O(*E*11)	0·8041 (1)	0·8593 (1)	0·6169 (1)	1·92 (2)
O(*E*12)	0·3890 (1)	0·0444 (1)	0·2109 (1)	1·81 (2)
O(*L*12)	0·0719 (1)	0·8663 (1)	0·1227 (1)	1·68 (2)
O(*E*21)	0·8098 (2)	0·5983 (1)	0·9602 (1)	2·15 (2)
O(*E*22)	0·2438 (1)	0·1015 (1)	0·9012 (1)	2·01 (2)
O(*L*21)	0·8694 (1)	0·8283 (1)	0·8667 (1)	1·51 (2)
O(7)	0·3388 (2)	0·3789 (1)	0·7667 (1)	2·54 (2)
O(8)	0·7412 (2)	0·5231 (2)	0·4178 (1)	3·18 (3)
O(9)	0·3603 (2)	0·7754 (2)	0·3605 (1)	2·74 (2)
O(10)	0·9063 (2)	0·4306 (2)	0·7291 (1)	2·76 (2)
N(1)	0·6233 (2)	0·3092 (2)	−0·0066 (1)	1·80 (2)
N(2)	0·2961 (2)	−0·0058 (2)	0·6110 (1)	1·76 (2)
C(11)	0·6794 (2)	0·3230 (2)	0·1559 (2)	1·93 (3)
C(12)	0·6911 (2)	0·5060 (2)	0·2718 (2)	1·82 (2)
C(21)	0·1592 (2)	0·8211 (2)	0·5048 (2)	1·94 (3)
C(22)	0·2183 (2)	0·7198 (2)	0·3715 (2)	1·70 (2)

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in glycine cyclo-tetraphosphate; e.s.d.'s are given in parentheses*

P(1)	O(*L*12)	O(*L*21)	O(*E*11)	O(*E*12)
O(*L*12)	1·6118 (8)	2·505 (1)	2·526 (1)	2·464 (1)
O(*L*21)	102·66 (5)	1·596 (1)	2·471 (1)	2·549 (1)
O(*E*11)	109·10 (6)	106·48 (6)	1·487 (1)	2·573 (2)
O(*E*12)	105·49 (5)	111·70 (7)	120·05 (6)	1·483 (1)

P(2)	O(*L*12)	O(*L*21)	O(*E*21)	O(*E*22)
O(*L*12)	1·5989 (9)	2·460 (1)	2·465 (1)	2·540 (1)
O(*L*21)	100·18 (6)	1·608 (1)	2·462 (1)	2·557 (2)
O(*E*21)	105·99 (6)	105·36 (6)	1·487 (1)	2·563 (1)
O(*E*22)	111·38 (5)	112·07 (7)	119·86 (7)	1·475 (1)

P(1)–P(2)	2·9863 (5)	P(1)–O(*L*21)–P(2)	137·54 (7)
P(1)–P(2)	2·9412 (4)	P(1)–O(*L*12)–P(2)	132·72 (7)
P(2)–P(1)–P(2)	84·22 (1)	P(1)–P(2)–P(1)	95·78 (1)
N(1)–C(11)	1·481 (2)	N(1)–C(11)–C(12)	110·1 (1)
C(11)–C(12)	1·511 (2)	C(11)–C(12)–O(7)	123·2 (1)
C(12)–O(7)	1·201 (2)	C(11)–C(12)–O(8)	111·8 (1)
C(12)–O(8)	1·316 (2)	O(7)–C(12)–O(8)	125·0 (1)
O(7)–O(8)	2·234 (2)		
N(2)–C(21)	1·473 (1)	N(2)–C(21)–C(22)	110·2 (1)
C(21)–C(22)	1·508 (2)	C(21)–C(22)–O(9)	123·0 (1)
C(22)–O(9)	1·203 (2)	C(21)–C(22)–O(10)	111·1 (1)
C(22)–O(10)	1·312 (1)	O(9)–C(22)–O(10)	125·9 (1)
O(9)–O(10)	2·240 (2)		

	O(N)–H	H···O	O(N)···O	O(N)H···O
O(8)–H(1)···O(*E*11)	0·90 (3)	1·76 (3)	2·653 (1)	178 (3)
O(10)–H(2)···O(*E*21)	0·89 (3)	1·68 (3)	2·567 (2)	177 (2)
N(1)–H(N11)···O(*E*21)	0·87 (2)	1·96 (3)	2·817 (2)	169 (2)
N(1)–H(N12)···O(*E*12)	0·90 (2)	2·00 (2)	2·883 (1)	165 (2)
N(1)–H(N13)···O(*E*22)	0·87 (2)	2·28 (2)	2·957 (1)	135 (2)
N(2)–H(N21)···O(*E*22)	0·87 (3)	1·97 (3)	2·800 (2)	159 (3)
N(2)–H(N22)···O(*E*11)	0·86 (3)	2·15 (3)	2·918 (2)	148 (2)
N(2)–H(N23)···O(*E*12)	0·90 (3)	1·95 (3)	2·798 (2)	157 (3)

monochromator. Systematic absences: none. 14 reflections ($10 < \theta < 15{\cdot}5°$) for refining unit-cell dimensions. ω scan. 4494 reflexions collected: ($3 < \theta < 25°$), $\pm h \pm k, l$, $h_{max} = 13$, $k_{max} = 14$, $l_{max} = 14$. Scan width: 1·20°, scan speed: 0·02° s^{-1}, total background measuring time: 20 s. Two intensity and orientation (410 and $\bar{4}\bar{1}0$) reference reflections (no variation). Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods (*MULTAN*77; Main, Lessinger, Woolfson, Germain & Declercq, 1977). H atoms from difference-Fourier map. Anisotropic full-matrix least-squares refinement (on F), isotropic for H atoms. Unit weights. Final refinement cycles with 3393 reflexions corresponding to $I > 3\sigma_I$. Final $R = 0{\cdot}025$ ($wR = 0{\cdot}030$). $S = 0{\cdot}424$. Max. $\Delta/\sigma = 0{\cdot}06$ [B_{iso} of H(N13)]. Max. peak height in final difference-Fourier synthesis: 0·357 e Å^{-3}. No extinction correction. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. Computer used: Microvax-II.

Discussion. Table 1 reports the final atomic coordinates, while Table 2 gives the main interatomic distances and bond angles of the inorganic and organic groups and geometrical details of the hydrogen-bond scheme. Fig. 1 is a projection of the atomic arrangement along the *a* axis.*

This compound is the second example of a glycine condensed phosphate. The first is a glycine *cyclo*-triphosphate: $(C_2H_6NO_2)_3P_3O_9$ (Averbuch-Pouchot *et al.*, 1988). As for the previous compound, the phosphoric group is non-acidic, $(P_4O_{12})^{4-}$. The ring anions are centrosymmetric and located around the cell origin. The main geometric features of this anion are quite similar to those found for inorganic *cyclo*-tetraphosphates.

Two crystallographically independent glycine groups exist in the atomic arrangement. For both, the carboxylic group is not deprotonated and so their configuration is $(NH_3CH_2COOH)^+$. In the hydrogen-bond scheme

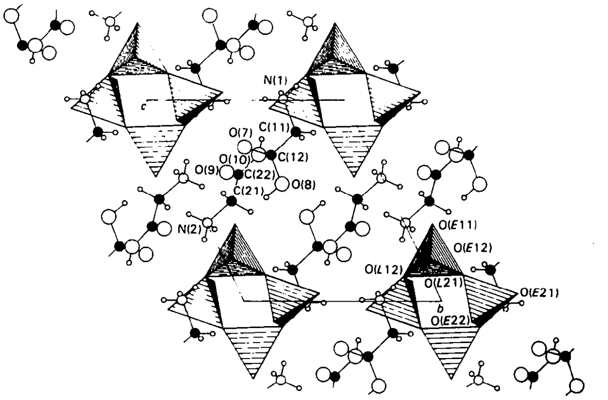

Fig. 1. Projection along the *a* axis of the atomic arrangement of $(NH_3CH_2COOH)_4P_4O_{12}$.

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44677 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

two main points should be noticed: there is no intermolecular bonding between the organic groups; only the external O atoms of the P_4O_{12} ring are involved in hydrogen bonds. Each glycine group is connected by hydrogen bonds to three different phosphoric groups.

References

AVERBUCH-POUCHOT, M. T., DURIF, A. & GUITEL, J.-C. (1988). *Acta Cryst.* C**44**, 99–102.
BOULLÉ, A. (1941). *C. R. Acad. Sci.* **206**, 517–519.
Enraf–Nonius (1977). *Structure Determination Package*, version RSX11M. Enraf–Nonius, Delft, The Netherlands.
International Tables for X-ray Crystallography (1974). Vol. IV, Table 2-2B. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Acta Cryst. (1988). C**44**, 890–892

Structure of L-Histidinium Dihydrogenmonophosphate Monohydrate

BY M. T. AVERBUCH-POUCHOT, A. DURIF AND J. C. GUITEL

Laboratoire de Cristallographie, associé à l'USTMG, Centre National de la Recherche Scientifique, 166 X, 38042 Grenoble CEDEX, France

(*Received* 2 *September* 1987; *accepted* 20 *January* 1988)

Abstract. $C_6H_{10}N_3O_2^+.H_2PO_4^-.H_2O$, $M_r = 271\cdot17$, orthorhombic, $P2_12_12_1$, $a = 8\cdot923\ (5)$, $b = 14\cdot383\ (9)$, $c = 8\cdot362\ (5)$ Å, $V = 1073\ (2)$ Å^3, $Z = 4$, $D_x = 1\cdot678$ Mg m^{-3}, $\lambda(\mathrm{Ag}\ K\alpha) = 0\cdot5608$ Å, $\mu = 0\cdot163$ mm^{-1}, $F(000) = 568$, $T = 293$ K, final $R = 0\cdot036$ for 2024 independent observed reflexions. Planes of $C_6H_{10}N_3O_2^+$ groups perpendicular to the *b* axis alternate with planes containing $H_2PO_4^-$ groups and water molecules. The $H_2PO_4^-$ groups are linked by hydrogen bonds to form infinite chains, which are themselves interconnected with the histidine planes through several other hydrogen bonds.

Introduction. Recently the first phosphate salt of L-histidine was described (Blessing, 1986). This salt has a 1:2 stoichiometry corresponding to the formula His.$2H_3PO_4$. The compound is in fact a 1:1 salt syncrystallized with a molecule of orthophosphoric acid and must be formulated as $HisH^+.H_2PO_4^-.H_3PO_4$. In the present work we describe the chemical preparation and the crystal structure of the monohydrate of the 1:1 salt: $C_6H_{10}N_3O_2^+.H_2PO_4^-.H_2O$.

Experimental. Crystals of the title compound have been prepared by mixing two dilute aqueous solutions of L-histidine and H_3PO_4 so as to obtain an equimolar ratio in the resulting solution. This solution is then kept at room temperature until a dry solid gel is obtained (2 to 3 months). Then a few drops of distilled water are added every day over several weeks, until some small crystalline areas dispersed in the gel appear. At this step, daily additions of larger quantities of water accelerate the crystallization. After additional weeks large orthorhombic prisms, up to 8 mm long, are obtained. Density not measured. $0\cdot42 \times 0\cdot30 \times 0\cdot30$ mm prism fragment Philips PW 1100 diffractometer, graphite monochromator. Systematic absences: $h00$: $h = 2n$; $0k0$: $k = 2n$; $00l$: $l = 2n$. 16 reflexions ($10\cdot5 < \theta < 16°$) for refining unit-cell dimensions. ω scan. Scan width: 1·20°, scan speed: 0·025° s^{-1}, total background measuring time: 10 s. 2708 reflexions measured ($3 < \theta < 30°$), h,k,l, $h_{\max} = 15$, $k_{\max} = 23$, $l_{\max} = 15$.

Two intensity and orientation reference reflexions every 2 h (250 and $\bar{2}\bar{5}0$): no significant variation. Lorentz and polarization corrections, no absorption correction. Direct methods (*MULTAN*77, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1977) used for structure determination. Anisotropic full-matrix least-squares refinement (on *F*) for non-H atoms, isotropic for H atoms. H atoms located by difference Fourier map. Unit weights. Final refinement with 2024 reflexions ($I > 4\sigma_I$). Final $R = 0\cdot036$ ($wR = 0\cdot038$), $S = 0\cdot607$, max. $\Delta/\sigma = 0\cdot07$. Max. peak height in final difference Fourier synthesis 0·42 e Å^{-3}. No extinction correction. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. Computer used: VAX 780.

Discussion. Table 1 reports the final atomic coordinates* and Fig. 1 is a projection along the *c* axis of the atomic arrangement.

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and distances and angles involving H have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44708 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/88/050890-03$03.00