TADEUSZ LIS

(1); Kuma KM-4 software for (2). For both compounds, program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1147). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Potassium D-3-Phosphoglycerate and Cyclohexylammonium D-3-Phosphoglycerate Hydrate

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Abstract

The structures of the D-3-phosphoglycerate monoanions in the potassium [KH$_2$(3-PGA)] and cyclohexylammonium [(CHA)H$_2$(3-PGA)] salts [H$_2$(3-PGA) = $^-$HO$_3$POCH$_2$CH(OH)(CO$_2$H)] have been determined by X-ray analysis at 297 and 85 K, respectively. The C—C—C—OH torsion angles which define the relationship of the carboxylic group to the carbon backbone are −120.2 (2) and 60.1 (3)°, and the P—O(ester) bond lengths are 1.596 (2) and 1.600 (2) Å for KH$_2$(3-PGA) and (CHA)H$_2$(3-PGA), respectively. There are extensive networks of hydrogen bonds in both crystals in which all H atoms of the hydroxyl and ammonium groups are involved. The K$^+$ ion is octacoordinate.

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Comment

The phosphate ester D-3-phosphoglycerate (3-PGA) is an essential intermediate in photosynthesis and glycolysis, as well as being a major building block in various biosynthetic pathways (Harper, Rodwell & Mayes, 1979). Knowledge of the three-dimensional structures of 3-PGA anions may be helpful, therefore, for complete interpretation of their interactions with macromolecules.

Unfortunately, up to now only three structures, all containing dianionic D-3-phosphoglycerate, have been published: disodium D-3-phosphoglycerate (Fewster & Fenn, 1982), barium D-3-phosphoglycerate dihydrate (Kamiya, Cruse & Kennard, 1983) and cadmium D-3-phosphoglycerate trihydrate (Mostad & Rosenqvist, 1971). In order to assess the influence of pH and chemical environment on the geometry of phosphoglycerates, we have begun a study of a number of crystal structures containing these anions in different ionization states. In this paper, the crystal structures of the potassium and cyclohexylammonium salts of monoionized phosphoglycerate, KH$_2$(3-PGA) and (CHA)H$_2$(3-PGA), respectively, are reported.
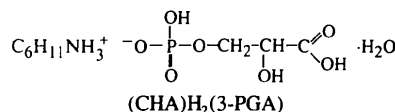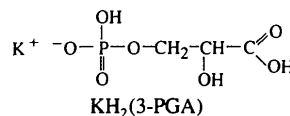
The KH$_2$(3-PGA) crystal consists of phosphoglycerate monoanions and potassium cations whereas the (CHA)H$_2$(3-PGA) crystal is built up from phosphoglycerate monoanions, cyclohexylammonium cations and water of hydration. In each structure, the O(2) hydroxyl atom lies close to the plane of the adjacent carboxylic group. The main conformational difference between the two monoanions is in the relationship of O(2) to the carboxylic hydroxyl group, O(1)H (Figs. 1 and 2): O(1) and O(2) are *syn* in KH$_2$(3-PGA) but *anti* in (CHA)H$_2$(3-PGA). As a result, the C—C—C—O(1) torsion angle, which defines the twist of the carboxylic group with respect to the glycerate residue, is −120.2 (2)° in KH$_2$(3-PGA) and 60.1 (3)° in (CHA)H$_2$(3-PGA).

The geometry of the phosphate groups (Tables 2 and 4) does not depart from that commonly found in other monophosphate organic esters (Starynowicz, 1986; Lis & Jerzykiewicz, 1993; Jerzykiewicz & Lis, 1994). The ester P—O bond lengths of 1.596 (2) Å in KH$_2$(3-PGA) and 1.600 (2) Å in (CHA)H$_2$(3-PGA) are characteristic of monoionized phosphate. The orientation of the phosphate group with respect to the atom C(2) is almost *trans* in both structures, as shown by the P—O—C—C torsion angles (Tables 2 and 4).
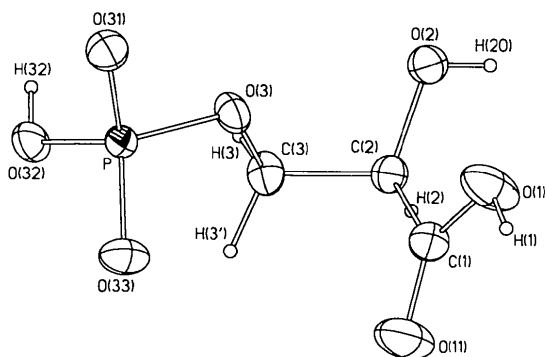
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Fig. 1. The structure and numbering scheme of the D-3-phospoglycerate monoanion in KH₂(3-PGA). Displacement ellipsoids are plotted at the 50% probability level.

Fig. 2. The structure and numbering scheme of the D-3-phospoglycerate monoanion in (CHA)H₂(3-PGA). Displacement ellipsoids are plotted at the 50% probability level.

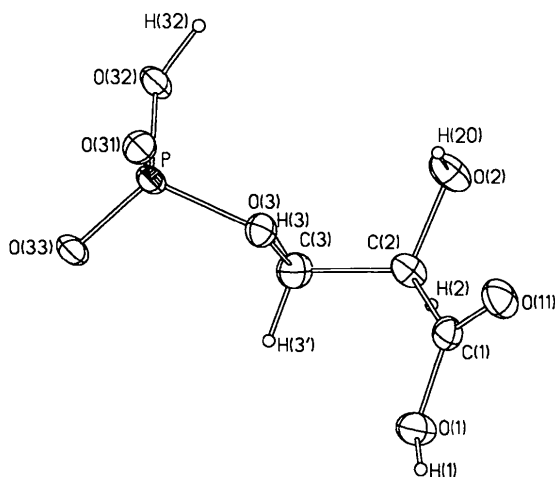Fig. 3. The packing arrangement in the crystal of KH₂(3-PGA).
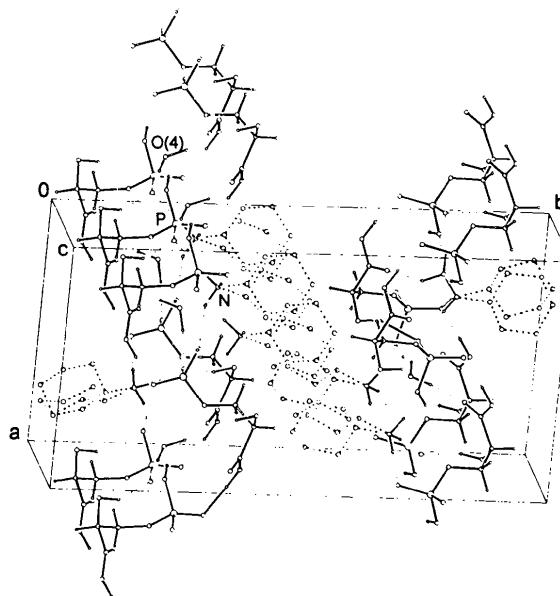
Fig. 4. The packing arrangement in the crystal of (CHA)H₂(3-PGA).

The crystal packing in (CHA)H₂(3-PGA) involves hydrophilic layers perpendicular to the *b* axis, composed of the D-3-phosphoglycerate monoanions, ammonium groups and water molecules. These layers are separated by hydrophobic regions formed by cyclohexyl rings (Fig. 4).

The D-3-phosphoglycerate monoanions are linked to each other by strong hydrogen bonds between carboxylic groups (donors) and the phosphate groups (acceptors) [2.596 (3) Å] as well as by weak hydrogen bonds between the hydroxy O(2) and phosphate O(33) atoms [2.842 (3) Å]. Furthermore, three phosphate groups are bridged by one cyclohexylammonium cation via hydrogen bonds of 2.794 (3)–2.866 (3) Å. The water molecule is the acceptor of the shortest hydrogen bond from a phosphate group [2.536 (3) Å] and is donor to the phosphate and carboxylic groups.

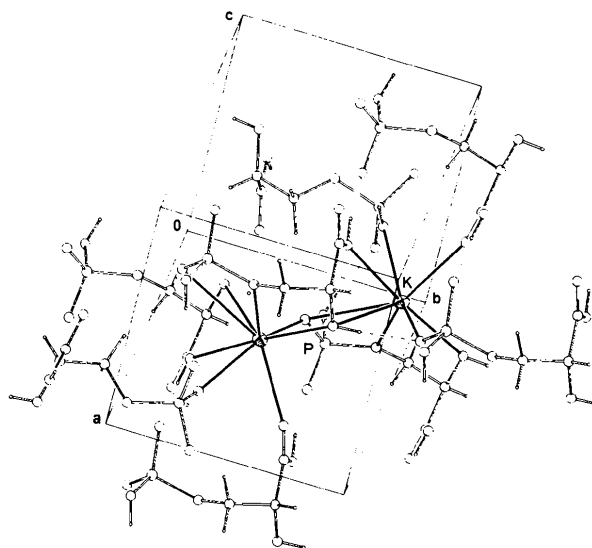In the hydrophobic region, the outer portions of the cyclohexyl rings attached to ammonium groups situated

in neighbouring hydrophilic layers are adjacent, though the shortest intermolecular distances between these rings are still long. As a result of this loose packing, the cyclohexyl rings are disordered (see *Experimental*).

The crystal structure of KH₂(3-PGA) appears to be governed by the coordination around the potassium cation (Fig. 3), which has eight O neighbours [K—O distances 2.699 (2)–3.411 (2) Å (Fig. 3)]. The K⁺ ion is attached to O(2), O(3) and O(31) of one monoanion, and to O(1ⁱⁱⁱ) and O(2ⁱⁱⁱ) of a second. The coordination of the K⁺ ion is completed by the

atoms O(32^{iv}), O(31^{ii}) and O(11^{i}). Consequently, each monoanion is coordinated to five K$^+$ cations. The structure is also stabilized by three independent hydrogen bonds between hydroxy groups and the phosphate O atoms [O(1)—H(1)$\cdots$O(33^{v}), O(32)—H(32)$\cdots$O(33^{vi}), O(2)—H(20)$\cdots$O(31^{vii})]. The main role in this network is played by O(33), the only O atom not coordinated to a K$^+$ ion, which strongly bonds (as acceptor) to hydroxy groups of two symmetry related anions [O(1)$\cdots$O(33^{v}) 2.579 (2) and O(32)$\cdots$O(33^{vi}) 2.573 (2) Å].

Experimental

Commercially available (Sigma) tri(cyclohexylammonium) D-3-phosphoglycerate [(CHA)$_3$(3-PGA)] was passed over Dowex 50W(H$^+$) resin. Colourless crystals of the title compounds were grown by slow concentration of aqueous solutions containing a 1:1 molar ratio of D-3-phosphoglyceric acid and KOH or cyclohexylamine. The density D_m of the crystal of KH$_2$(3-PGA) was measured by flotation in C$_2$H$_4$Br$_2$/CCl$_4$, and that of the crystal of (CHA)H$_2$(3-PGA) by flotation in C$_6$H$_5$Cl/CCl$_4$.

KH$_2$(3-PGA)

Crystal data

K$^+$.C$_3$H$_6$O$_7$P$^-$	Mo $K\alpha$ radiation
M_r = 224.15	λ = 0.71069 Å
Orthorhombic	Cell parameters from 25
$P2_12_12_1$	reflections
a = 7.349 (3) Å	θ = 10–12°
b = 7.535 (3) Å	μ = 0.857 mm^{-1}
c = 14.539 (5) Å	T = 297 (2) K
V = 805.1 (6) Å^3	Prism
Z = 4	0.5 × 0.5 × 0.3 mm
D_x = 1.849 (2) Mg m^{-3}	Colourless
D_m = 1.850 Mg m^{-3}	

Data collection

Kuma KM-4 diffractometer	θ_{max} = 32.5°
$\omega/2\theta$ scans	h = 0 → 11
Absorption correction:	k = 0 → 11
none	l = 0 → 21
3792 measured reflections	3 standard reflections
2903 independent reflections	monitored every 100
2694 observed reflections	reflections
[$I > 2\sigma(I)$]	intensity decay: 3%
R_{int} = 0.0187	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max}$ = 0.001
$R(F)$ = 0.0264	$\Delta\rho_{max}$ = 0.594 e Å^{-3}
$wR(F^2)$ = 0.0703	$\Delta\rho_{min}$ = −0.326 e Å^{-3}
S = 1.131	Extinction correction: none
2903 reflections including	Atomic scattering factors
1008 Friedel pairs	from *International Tables*
133 parameters	*for Crystallography* (1992,
$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2$	Vol. C, Tables 4.2.6.8 and
$+ 0.0726P]$	6.1.1.4)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for* KH$_2$(3-PGA)

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

	x	y	z	U_{eq}
K	0.39163 (4)	0.99360 (5)	0.68244 (2)	0.03047 (8)
P	0.76067 (4)	0.72300 (4)	0.58337 (2)	0.01786 (7)
O(1)	0.84784 (18)	1.23258 (25)	0.74708 (9)	0.0438 (4)
O(11)	1.08026 (18)	1.17645 (24)	0.65218 (10)	0.0455 (4)
O(2)	0.60906 (14)	1.27506 (14)	0.61210 (8)	0.0271 (2)
O(3)	0.70359 (14)	0.92690 (12)	0.59080 (8)	0.0252 (2)
O(31)	0.62852 (15)	0.62741 (14)	0.64365 (8)	0.0275 (2)
O(32)	0.74028 (15)	0.67426 (14)	0.47852 (7)	0.0262 (2)
O(33)	0.96019 (15)	0.70001 (17)	0.60539 (7)	0.0295 (3)
C(1)	0.9210 (2)	1.2108 (2)	0.66532 (10)	0.0265 (3)
C(2)	0.7883 (2)	1.2317 (2)	0.58501 (10)	0.0220 (3)
C(3)	0.7841 (3)	1.0594 (2)	0.53088 (9)	0.0247 (3)

Table 2. *Selected geometric parameters (Å, °) for* KH$_2$(3-PGA)

P—O(3)	1.596 (2)	C(1)—O(11)	1.214 (2)
P—O(31)	1.493 (2)	K—O(3)	2.699 (2)
P—O(32)	1.575 (2)	K—O(11^i)	2.707 (2)
P—O(33)	1.511 (2)	K—O(31^{ii})	2.726 (2)
C(1)—C(2)	1.529 (2)	K—O(1^{iii})	2.831 (2)
C(2)—C(3)	1.519 (2)	K—O(2)	2.845 (2)
C(2)—O(2)	1.413 (2)	K—O(32^{iv})	2.883 (2)
C(3)—O(3)	1.451 (2)	K—O(31)	3.311 (2)
C(1)—O(1)	1.315 (2)	K—O(2^{iii})	3.411 (2)
O(31)—P—O(3)	104.7 (1)	C(3)—C(2)—C(1)	108.7 (2)
O(32)—P—O(3)	105.4 (1)	O(1)—C(1)—C(2)	114.6 (2)
O(33)—P—O(3)	110.6 (1)	O(11)—C(1)—C(2)	121.1 (2)
O(31)—P—O(32)	113.2 (1)	O(2)—C(2)—C(3)	108.8 (2)
O(31)—P—O(33)	116.8 (1)	O(2)—C(2)—C(1)	113.9 (2)
O(33)—P—O(32)	105.7 (1)	O(3)—C(3)—C(2)	106.6 (2)
C(3)—O(3)—P	120.9 (1)	O(1)—C(1)—O(11)	124.3 (2)

O(31)—P—O(3)—C(3)	−170.8 (2)
O(32)—P—O(3)—C(3)	−51.2 (2)
O(33)—P—O(3)—C(3)	62.5 (2)
P—O(3)—C(3)—C(2)	−149.2 (2)
O(2)—C(2)—C(3)—O(3)	−58.0 (2)
C(1)—C(2)—C(3)—O(3)	66.6 (2)
O(1)—C(1)—C(2)—C(3)	−120.2 (2)
O(11)—C(1)—C(2)—C(3)	59.6 (2)
O(1)—C(1)—C(2)—O(2)	1.3 (2)
O(11)—C(1)—C(2)—O(2)	−178.8 (2)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O(1)—H(1)$\cdots$O(33^v)	0.86 (3)	1.75 (3)	2.579 (2)	164 (3)
O(32)—H(32)$\cdots$O(33^{vi})	0.85 (4)	1.73 (4)	2.573 (2)	170 (4)
O(2)—H(20)$\cdots$O(31^{vii})	0.81 (3)	1.89 (3)	2.698 (2)	174 (3)

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

(CHA)H$_2$(3-PGA)

Crystal data (at 292 K in square brackets)

C$_6$H$_{14}$N$^+$.C$_3$H$_6$O$_7$P$^-$.H$_2$O	Mo $K\alpha$ radiation
M_r = 303.25	λ = 0.71069 Å
Orthorhombic	Cell parameters from 52 [25]
$P2_12_12$	reflections
a = 11.332 (6) [11.316 (9)] Å	θ = 10 [10]–12 [16]°
b = 22.406 (11)	μ = 0.220 mm^{-1}
[22.63 (2)] Å	T = 85 (2) [292 (1)] K
c = 5.783 (3) [5.852 (7)] Å	Plate

$V = 1468.3\,(13)$
$[1499\,(3)]\ \text{Å}^3$
$Z = 4$
$D_x = 1.372\,(2)$
$[1.344\,(3)]\ \text{Mg m}^{-3}$
$D_m = [1.36]\ \text{Mg m}^{-3}$

$0.5 \times 0.3 \times 0.06$ mm
Colourless

Data collection

Kuma KM-4 diffractometer
$\omega/2\theta$ scans
Absorption correction:
  none
4050 measured reflections
3551 independent reflections
2667 observed reflections
  $[I > 2\sigma(I)]$
$R_{int} = 0.0186$

$\theta_{max} = 30°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 29$
$l = 0 \rightarrow 8$
3 standard reflections
  monitored every 100
  reflections
  intensity decay: 3%

Refinement

Refinement on F^2
$R(F) = 0.0433$
$wR(F^2) = 0.1037$
$S = 1.061$
2667 reflections including
  1018 Friedel pairs
259 parameters
$w = 1/[\sigma^2(F_o^2) + (0.064P)^2 + 0.32P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.117$
$\Delta\rho_{max} = 0.474\ \text{e Å}^{-3}$
$\Delta\rho_{min} = -0.243\ \text{e Å}^{-3}$
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 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (CHA)H₂(3-PGA)

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

	x	y	z	U_{eq}
P	0.05405 (6)	0.24508 (3)	0.17515 (11)	0.0177 (2)
O(1)	0.3855 (2)	0.12668 (10)	−0.0680 (4)	0.0254 (5)
O(11)	0.3259 (2)	0.16392 (10)	−0.4093 (4)	0.0274 (5)
O(2)	0.1038 (2)	0.11975 (10)	−0.3497 (4)	0.0277 (5)
O(3)	0.1406 (2)	0.20571 (9)	0.0185 (4)	0.0200 (5)
O(31)	0.0741 (2)	0.30801 (9)	0.0973 (4)	0.0222 (5)
O(32)	−0.0745 (2)	0.22332 (10)	0.1111 (4)	0.0206 (5)
O(33)	0.0727 (2)	0.23160 (9)	0.4266 (3)	0.0226 (5)
O(4)	−0.1260 (2)	0.23767 (10)	−0.3121 (4)	0.0242 (4)
C(1)	0.3066 (3)	0.13780 (13)	−0.2319 (5)	0.0192 (6)
C(2)	0.1849 (3)	0.11324 (13)	−0.1676 (6)	0.0223 (6)
C(3)	0.1432 (3)	0.14197 (14)	0.0537 (6)	0.0235 (7)
N	0.2061 (2)	0.31417 (10)	0.6898 (5)	0.0182 (5)
C(4)†	0.2555 (9)	0.3740 (5)	0.6295 (16)	0.022 (2)
C(5)†	0.2950 (8)	0.4060 (4)	0.8502 (14)	0.026 (2)
C(6)†	0.3471 (9)	0.4666 (5)	0.7803 (18)	0.039 (3)
C(7)†	0.2625 (14)	0.5027 (5)	0.6351 (18)	0.038 (3)
C(8)†	0.2225 (10)	0.4677 (4)	0.4219 (14)	0.042 (2)
C(9)†	0.1688 (9)	0.4071 (4)	0.4943 (17)	0.036 (2)
C(41)‡	0.2092 (8)	0.3758 (4)	0.5873 (14)	0.022 (2)
C(51)‡	0.3072 (8)	0.4120 (4)	0.7074 (24)	0.065 (4)
C(61)‡	0.3154 (9)	0.4760 (5)	0.6089 (23)	0.066 (4)
C(71)‡	0.1946 (10)	0.5057 (5)	0.6378 (20)	0.055 (3)
C(81)‡	0.1032 (7)	0.4702 (4)	0.4987 (16)	0.050 (2)
C(91)‡	0.0963 (6)	0.4065 (3)	0.6014 (14)	0.039 (2)

† Site occupancy = 0.566 (7).
‡ Site occupancy = 0.434 (7).

Table 4. *Selected geometric parameters* $(\text{Å},\ °)$ *for* (CHA)H₂(3-PGA)

P—O(3)	1.600 (2)	C(2)—C(3)	1.509 (4)
P—O(31)	1.497 (2)	C(1)—C(2)	1.531 (4)
P—O(33)	1.500 (2)	C(2)—O(2)	1.405 (4)
P—O(32)	1.580 (2)	C(1)—O(1)	1.327 (4)
C(3)—O(3)	1.443 (4)	C(1)—O(11)	1.201 (3)
O(31)—P—O(3)	104.8 (2)	O(3)—C(3)—C(2)	108.0 (2)
O(32)—P—O(3)	105.2 (2)	C(3)—C(2)—C(1)	109.6 (2)
O(33)—P—O(3)	110.6 (2)	O(2)—C(2)—C(3)	112.7 (2)
O(31)—P—O(32)	111.1 (2)	O(2)—C(2)—C(1)	111.7 (2)
O(31)—P—O(33)	117.3 (2)	O(1)—C(1)—C(2)	111.5 (2)
O(32)—P—O(33)	107.2 (2)	O(11)—C(1)—C(2)	123.2 (3)
C(3)—O(3)—P	118.6 (2)	O(11)—C(1)—O(1)	125.4 (3)

O(31)—P—O(3)—C(3)	179.3 (2)
O(32)—P—O(3)—C(3)	−63.4 (2)
O(33)—P—O(3)—C(3)	51.9 (2)
P—O(3)—C(3)—C(2)	155.5 (2)
O(2)—C(2)—C(3)—O(3)	−67.1 (3)
O(1)—C(1)—C(2)—O(2)	−174.3 (2)
O(11)—C(1)—C(2)—O(2)	6.0 (4)
O(1)—C(1)—C(2)—C(3)	60.1 (3)
O(11)—C(1)—C(2)—C(3)	−119.7 (3)
C(1)—C(2)—C(3)—O(3)	58.0 (3)

D—H···A	H···A	D···A	D—H···A
O(1)—H(1)···O(31^i)	1.63 (3)	2.596 (3)	175 (3)
O(2)—H(20)···O(33^{ii})	1.96 (3)	2.842 (3)	150 (4)
O(32)—H(32)···O(4)	1.58 (3)	2.536 (3)	167 (5)
O(4)—H(40)···O(11^{iii})	2.07 (5)	2.785 (3)	129 (4)
O(4)—H(401)···O(33^{ii})	1.76 (3)	2.715 (3)	170 (3)
N—H(11)···O(32^{iv})	1.95 (3)	2.866 (3)	152 (3)
N—H(12)···O(33)	1.84 (5)	2.833 (3)	171 (4)
N—H(13)···O(31^v)	1.80 (3)	2.794 (3)	175 (3)

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

The space groups and approximate unit-cell dimensions were initially determined from oscillation and Weissenberg photographs.

For the (CHA)H₂(3-PGA) salt, initially, a room-temperature data set was collected. However, most of the final displacement parameters for the cyclohexylammonium C atoms assumed very high values and the C—C bond lengths were rather unrealistic. We decided, therefore, to measure new intensity data at 85 K. A crystal fragment was cooled very rapidly with an Oxford Cryosystems Cryostream Cooler. During refinement of the 85 K data, each cyclohexylammonium ring C atom was found to be disordered between two adjacent positions with occupancy factors 0.434 (7) and 0.566 (7). The positions of C-bonded H atoms were calculated assuming typical stereochemistry and these atoms were refined using a riding model. Other H atoms were found from difference syntheses and refined with restraints for O—H (0.97 Å) and N—H (1.00 Å).

For both compounds, data collection: Kuma KM-4 software (Kuma, 1987); cell refinement: Kuma KM-4 software; data reduction: Kuma KM-4 software; program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976).

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Oxidation of 5,6-Diamino-1,3-dimethyluracil by Metal Ions: Structure of 1,3,6,8-Tetramethyl-2,4,7,9(1H,3H,6H,8H)-pyrimido[4,5-g]pteridinetetrone

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Abstract

The structure of the title compound, $C_{12}H_{12}N_6O_4$, consists of independent tricyclic molecules with a central pyrazine ring and terminal pyrimidine rings. The molecular centroid coincides with a crystallographic

inversion centre, leading to a *trans* disposition of the terminal pyrimidine rings. The angle between the central pyrazine ring and the pyrimidine rings is 4.2 (3)°, indicating that the molecule is almost planar.

Comment

Previous work has shown that some *N*-oxide compounds exhibit a number of remarkable photochemical properties (Sako, Nagai & Maki, 1993). These compounds can be prepared by the oxidation of amino or nitroso uracil derivatives with a metal ion and further reaction with $NaNO_2$ (Yoneda, Sakuma, Ichiba & Shinomura, 1976). With the aim of synthesizing new *N*-oxide compounds of this type, we have investigated the influence of different metal ions on the final product of the oxidative reaction. Since enediamines are readily oxidized, especially when they are conjugated with a carbonyl group, we have studied the oxidative reaction of the enediamine 5,6-diamino-1,3-dimethyluracil with a range of metal ions. It was already known that with Cu^{2+} the copper complex of the diamino ligand is obtained, whereas with Fe^{3+}, 1,3,6,8-tetramethyl-2,4,5,7(1H,3H,6H,8H)-pyrimido[5,4-g]pteridine-tetrone, in which the terminal pyridine rings are *cis*, is formed (Okamoto, Ogura, Kurasawa & Kinoshita, 1984). However, in boiling ethanol, the presence of one equivalent of Au^{3+}, Hg_2^{2+}, Ag^+ or Tl^{3+} gives the title compound, (I), in which the terminal pyrimidine rings are *trans*. Consequently, the type of metal ion used in the reaction is not mechanistically 'innocent' and the course of the reaction depends on the redox potential of the metal ion.

(I)
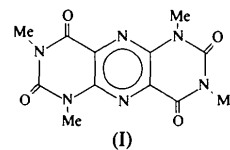
A drawing of the molecule is given in Fig. 1 together with the atomic labelling scheme. Crystals of the title compound contain centrosymmetric tricyclic molecules comprising a central pyrazine ring and terminal pyrimidine rings. Bond lengths and angles in the pyrimidine and pyrazine rings are within the ranges usually found for related pyrimidine and pyrazine derivatives (Otieno, Rettig, Thompson & Trotter, 1989; Fleischer, Jeter & Florian, 1974; Suárez-Varela, Legros, Galy, Colacio, Ruiz, López-González, León & Perona, 1989). The pyrimidine and pyrazine rings are essentially planar, with maximum deviations from the calculated mean plane of 0.084 (4) and 0.006 (4) Å, respectively. In the pyrimidine rings there are some steric interactions involving the exocyclic groups, as shown by the short C(1)···O(2^i), O(1)···C(1) and C(2)···O(1) contacts, which are 0.6 Å less than the sum of the