

Table 3 (cont.)

Molecule *A*, piperidine rings

	X	Y
C—N—C(1)	115.2 (7)	115.0 (8)
C—N—C(5)	116.5 (6)	113.5 (5)
C(1)—N—C(5)	111.3 (8)	112.7 (6)
N—C(1)—C(2)	111.0 (7)	110.1 (7)
C(1)—C(2)—C(3)	109.4 (7)	110.9 (1.0)
C(2)—C(3)—C(5)	111.0 (1.1)	111.9 (7)
C(3)—C(4)—C(5)	109.9 (8)	109.1 (8)

Table 4. Selected mean planes in (II)

Molecule *B*Plane *L*: C(4), N(1), N(2), C(7)—C(12)
 $10.3246x + 6.5210y + 1.6107z = 3.2874$ Plane *M*: C(2), C(3), C(5), C(6)
 $-13.1911x + 6.5092y + 9.0672z = 5.5720$ Molecule *A*Plane *N*: N(51), N(52), C(57)—C(62)
 $0.4150x - 4.6686y + 15.0215z = 2.4422$ Plane *O*: C(21), C(22), C(24), C(25)
 $10.3703x + 6.98037y - 11.3648z = 2.7031$ Plane *P*: C(31), C(32), C(34), C(35)
 $12.4612x + 5.7084y - 14.8678z = 6.8596$ Plane *Q*: C(52), C(53), C(55), C(56)
 $0.6833x + 7.4675y + 8.9196z = -3.3344$

Angles between planes (°)

<i>L</i> — <i>M</i>	75.42	<i>N</i> — <i>P</i>	134.28
<i>L</i> — <i>N</i>	92.16	<i>O</i> — <i>P</i>	12.64
<i>N</i> — <i>O</i>	132.16	<i>N</i> — <i>Q</i>	91.30

1.40 Å). This is a typical value for N adjacent to an aromatic ring, identical with C(60)—N(53) and C(61)—N(54) for the piperidine substituents in *A*. In *A* C(57)—N(51) and C(58)—N(52) are much shorter (1.300 Å) and C(57)—C(58) and C(60)—C(61)

average 1.494 Å, indicating little or no conjugation between the diene systems C(60)=C(59)—C(58)=N(52) and C(61)=C(62)—C(58)=N(51). N(51), N(52), C(51)—C(62) are all within 0.007 Å of the mean plane containing them; C(54) is 0.015 Å out of this plane.

One piperidine group lies on either side of the benzimidazole ring in *A*, connected to it equatorially. N(53) and N(54) are 0.031 Å above and below the benzimidazole plane. The normals to the mean planes C(21), C(22), C(24), C(25) and C(31), C(32), C(34), C(35) intersect at 12.6° and make angles to that of the benzimidazole plane of 134.3 and 132.1° respectively.

Equations for selected mean planes are given in Table 4.

Fig. 3 shows that there is no possibility of electronic interaction between the π systems of *A* and *B* in (II). In the related black complexes the absence of the bulky piperidine rings must allow the molecular planes of donor and acceptor to be parallel rather than at right angles as observed in (II).

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The Crystal Structure of Guanidinium Pyrophosphate Monoperhydrate Sesquihydrate

BY J. M. ADAMS AND VIJAYALAKSHMI RAMDAS

Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth SY23 1NE, Wales

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[C(NH₂)₃]₄P₂O₇·H₂O₂·1½H₂O crystallizes in space group *P2₁/a* with *a* = 17.84 (3), *b* = 14.15 (2), *c* = 17.72 (3) Å, β = 116.8 (2)°; each asymmetric unit consists of twice the above formula. The crystals are extremely stable carriers of hydrogen peroxide. There are two types of hydrogen-bonded chain in the structure: (···P₂O₇···H₂O···)_n and (···P₂O₇···H₂O₂···)_n. The remaining water molecules and the guanidinium ions hold these chains together. Each H₂O₂ molecule donates two hydrogen bonds and receives three.

Introduction

This study brings together two separate lines of investigation pursued in these laboratories: (i) multiple hydrogen bonding to O atoms through guanidinium cations and (ii) research into relatively stable perhydrates, *i.e.* compounds containing H₂O₂ of crystallization. It has already been suggested (Adams, Pritchard & Thomas, 1976) that it might be possible to design stable carriers of H₂O₂ by attempting to maximize the number of hydrogen bonds in the structure by the use of suitable cations and anions.

Many perhydrates are relatively unstable, decomposing typically in minutes or a few days under laboratory conditions. Further, there is often a marked dependence on humidity. Sodium percarbonate (Na₂CO₃·1½H₂O₂; Adams & Pritchard, 1977), for example, is stable for many months at a relative humidity of 50% but is decomposed rapidly at, say, 90% rh. Guanidinium pyrophosphate monoperhydrate sesquihydrate is, therefore, among the most stable perhydrates since after 7 d at 98% rh (293 K) over 60% of the original active oxygen is retained.*

Experimental

Colourless needles of the title compound were formed by evaporation of a solution made by dissolving guanidinium pyrophosphate monohydrate in 50% (w/w) H₂O₂. The presence of H₂O₂ within the crystals was tested by use of acid Ti^{IV} solutions and iodometrically. Guinier photographs were also used to test that one phase was produced consistently by the experimental procedures. Thermogravimetric analysis gave a total weight loss of 12.8% occurring in one single smooth curve (theoretical 12.85%) which was completed by 390 K. A complicated set of endotherms and exotherms was obtained from differential scanning calorimetry, typical of other perhydrates (*e.g.* Na₂CO₃·1½H₂O₂).

Cell parameters (Table 1) were determined from oscillation and Weissenberg photographs and were refined by a least-squares procedure. The systematic absences, $h0l$ $h = 2n$, $0k0$ $k = 2n$, corresponded to

* This compound proved, unfortunately, to be unstable under prolonged X-ray bombardment, necessitating the use of more than one crystal to collect intensities.

Table 1. *Crystal data*

$a = 17.84$ (3) Å	Space group: $P2_1/a$
$b = 14.15$ (2)	$Z = 4$
$c = 17.72$ (3)	$d_o = 1.55$ g cm ⁻³ (by flotation)
$\beta = 116.8$ (2)°	$d_c = 1.57$ g cm ⁻³
$\lambda(\text{Cu } K\alpha) = 1.5418$ Å	
Asymmetric unit: $2[\text{C}(\text{NH}_2)_3]_4\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$	

space group $P2_1/a$. Film packs (0–8 kl , 0–8 l and $hk0$) were used to collect intensities. The films were scanned and the intensities corrected for Lorentz and polarization effects and put on a common scale by the SRC Microdensitometer Service at the Atlas Computer Laboratory. Two separate sets of data were prepared. The films taken about **b** were considerably streaked* and hence those data had a poor R . One set of data, therefore, contained all the reflections while the other had only the data collected about **a** together with $h3l$ and $h5l$ which were used for scaling purposes.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All computations except the structure solution were undertaken with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Structure determination

The structure was solved from all 3277 measured intensities. The reflections too weak to be measured by the microdensitometer were added and given an F value equal to half the lowest observed F . A Wilson plot gave an overall temperature factor of 1.0 Å². The 350 planes with $E > 1.6$ were used to solve the structure with *MULTAN* 76 (Germain, Main & Woolfson, 1971). Despite the relatively large number of atoms in the asymmetric unit (56 non-hydrogen atoms) the structure solution proceeded smoothly and both the pyrophosphate anions in the asymmetric unit were easily recognized in an E map computed from the set of planes with the highest figure of merit. The other non-hydrogen atoms were located by successive difference syntheses. Refinement ceased (even with anisotropic thermal parameters) at $R = 0.18$ with this full data set.

At this stage further refinement was attempted with the better a axis data (together with $h3l$ and $h5l$). This brought R down to only 0.15. The use of different weighting schemes did not help, nor did a trial with sub-cell data for refinement. The data were examined for evidence of extinction effects and seven reflections were omitted (002, 005, 057, 406, 629, 800 and 802) which reduced R to 0.138. A further 19 reflections (marked with an asterisk in the structure factor tables) which were somewhat less severely affected by extinction were also removed from the refinement causing R to fall to 0.12. However, the temperature factors of some of the O atoms of one of the pyrophosphate groups became high. The effect was very pronounced on the bridge

* From preliminary work it was noted that photographs taken about **b** showed two characteristics: (i) the alternate layer lines were relatively weak, suggesting the possible presence of a sub-cell; (ii) although the $h0l$ photograph was free of streaking, on the levels with higher values of k there were streaks along the layer lines with odd h .

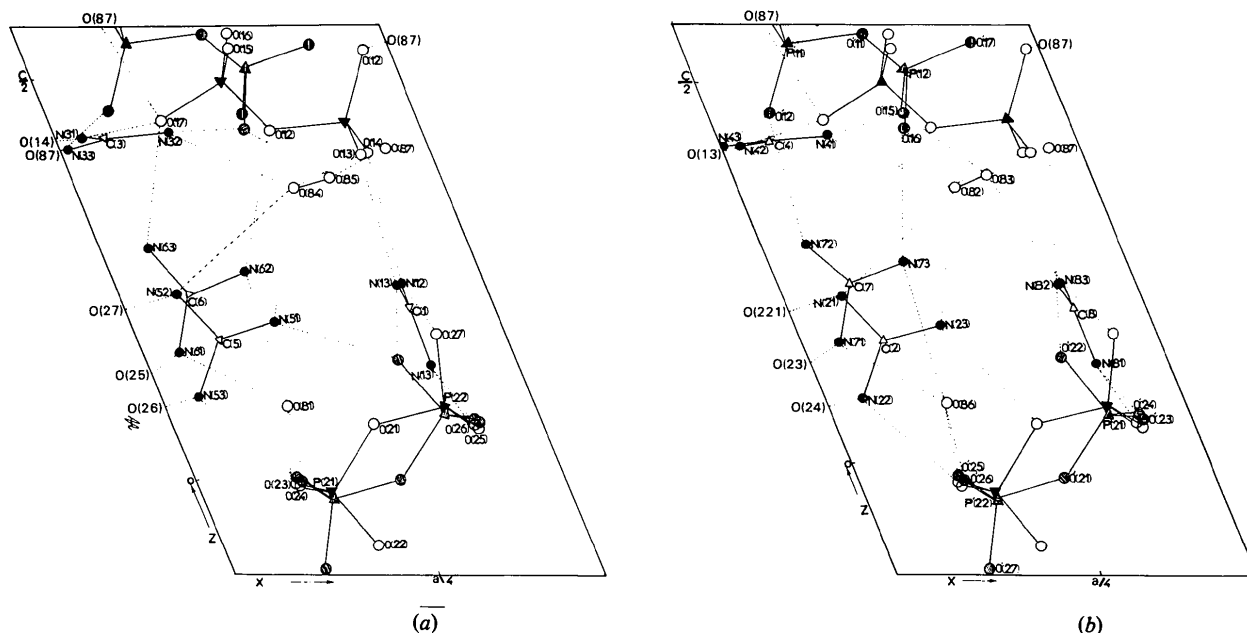


Fig. 1. Projections of part of the structure on to (010) showing in each case the pyrophosphate groups and the O(87) water molecule. Shown are (a) four of the eight guanidinium groups, one H₂O₂ and one H₂O molecule and (b) the remaining four guanidinium groups, H₂O₂ and H₂O molecules which are related to those shown in (a) by a non-crystallographic *b*/2 translation.

O(21) and the terminal O(22) and O(27). A difference map showed small but significant electron density peaks suggesting that part of this pyrophosphate group was inverted to occupy the same orientation as the equivalent pyrophosphate *b*/2 above. While new positions for O(21), O(22) and O(27) [*i.e.* O(211), O(221) and O(271)] could be obtained from the electron density map, the positions for the P atom and the other O atoms could not be distinguished (they overlapped the atoms of the non-inverted pyrophosphate). The positions for these atoms were calculated from the orientation of the pyrophosphate *b*/2 away. Refinement (including the site occupancy of these pyrophosphate groups) reduced *R* to 0.092 with site occupancy of 0.68 for the original pyrophosphate and 0.32 for the inverted orientation.*

It did not prove possible to locate the H atoms. Unit weights were used throughout. An (010) projection of part of the structure is shown in Fig. 1. The atomic coordinates and bond distances and angles are in Tables 2 and 3.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33354 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

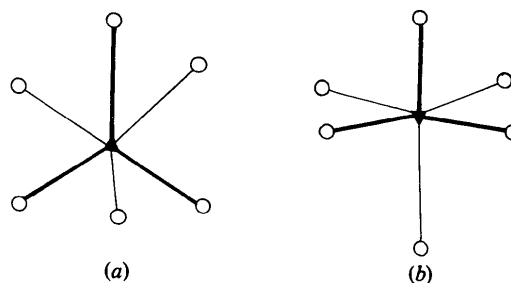


Fig. 2. Projections of pyrophosphate anions (a) PYR1 and (b) PYR2 on to (100) showing their different conformations.

Discussion

The pyrophosphate anion P(11), P(12) *etc.* (PYR1) is normal with a staggered conformation (Fig. 2); the bridge angle is usual at 131.6°. This group and those equivalent by symmetry ($\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$) are linked into infinite chains by H₂O₂ molecules (Fig. 3). The second pyrophosphate anion P(21), P(22) *etc.* (PYR2) is disordered between two orientations (with site occupancies 0.68, 0.32) which are related by a non-crystallographic twofold axis through the P atoms (Fig. 4). Equivalent pyrophosphate ions are again linked into infinite chains (Fig. 3) but this time by water molecules.

Table 2. Fractional atomic coordinates and their e.s.d.'s ($\times 10^4$)

	x	y	z
P(11)	3656 (2)	2457 (2)	4486 (2)
P(12)	2312 (3)	2426 (2)	5013 (2)
O(11)	2698 (6)	2543 (8)	4363 (5)
O(12)	4232 (5)	2430 (6)	5408 (5)
O(13)	3671 (7)	1564 (5)	4013 (6)
O(14)	3771 (7)	3333 (6)	4045 (6)
O(15)	2580 (8)	1480 (5)	5439 (7)
O(16)	2622 (8)	3241 (7)	5645 (7)
O(17)	1405 (6)	2464 (8)	4469 (6)
P(21)	1619 (5)	4734 (4)	9444 (4)
P(22)	3423 (5)	4752 (4)	10605 (3)
O(21)	2465 (11)	4706 (11)	10379 (8)
O(22)	1850 (11)	4691 (9)	8784 (6)
O(23)	1198 (11)	3862 (10)	9571 (9)
O(24)	1234 (12)	5635 (10)	9535 (10)
O(25)	3722 (10)	3869 (9)	10322 (9)
O(26)	3688 (11)	5660 (9)	10361 (9)
O(27)	3876 (10)	4736 (10)	11613 (9)
O(211)	2588 (34)	4737 (30)	9673 (26)
O(221)	1110 (20)	4687 (22)	8371 (18)
O(271)	3192 (24)	4700 (19)	11198 (15)
O(81)	1489 (8)	2272 (8)	638 (6)
O(86)	1441 (9)	7223 (9)	659 (7)
O(87)	5975 (6)	2527 (7)	5918 (6)
O(82)	2675 (9)	4671 (9)	3559 (8)
O(83)	3101 (10)	5537 (8)	3729 (7)
O(84)	2606 (8)	167 (8)	3536 (7)
O(85)	3154 (9)	-649 (7)	3712 (7)
C(1)	3500 (11)	2236 (10)	1919 (8)
N(11)	3474 (10)	1424 (8)	2284 (7)
N(12)	3545 (10)	3061 (8)	2317 (8)
N(13)	3504 (8)	2254 (8)	1186 (7)
C(2)	984 (14)	4506 (11)	1486 (10)
N(21)	711 (10)	4572 (9)	2116 (9)
N(22)	450 (9)	4295 (9)	724 (8)
N(23)	1795 (13)	4651 (11)	1731 (8)
C(3)	602 (18)	20 (9)	4189 (11)
N(31)	308 (9)	912 (8)	4233 (8)
N(32)	1394 (14)	-109 (9)	4296 (9)
N(33)	71 (10)	-719 (9)	4062 (8)
C(4)	587 (16)	4821 (12)	4186 (10)
N(41)	1347 (15)	4949 (8)	4254 (10)
N(42)	239 (11)	3941 (8)	4129 (8)
N(43)	34 (10)	5569 (8)	4080 (7)
C(5)	965 (13)	-489 (10)	1517 (10)
N(51)	1777 (12)	-366 (9)	1739 (8)
N(52)	672 (9)	-385 (8)	2119 (7)
N(53)	429 (9)	-698 (8)	746 (7)
C(6)	858 (13)	2037 (10)	2139 (9)
N(61)	404 (10)	1867 (9)	1325 (8)
N(62)	1645 (9)	2361 (10)	2416 (8)
N(63)	561 (11)	1917 (10)	2711 (9)
C(7)	897 (12)	7105 (9)	2308 (9)
N(71)	460 (10)	6877 (8)	1492 (8)
N(72)	565 (11)	6982 (10)	2848 (9)
N(73)	1652 (8)	7431 (11)	2571 (8)
C(8)	3510 (12)	7247 (10)	1942 (9)
N(81)	3501 (8)	7263 (8)	1202 (7)
N(82)	3460 (11)	8071 (9)	2295 (7)
N(83)	3460 (10)	6418 (8)	2288 (8)

Table 3. Bond lengths (Å) and angles (°)

P(11)—O(11)	1.626 (12)	P(11)—O(11)—P(12)	131.6 (5)
P(11)—O(12)	1.487 (8)	O(11)—P(11)—O(12)	108.2 (6)
P(11)—O(13)	1.523 (10)	O(11)—P(11)—O(13)	105.4 (6)
P(11)—O(14)	1.528 (11)	O(11)—P(11)—O(14)	104.2 (6)
P(12)—O(11)	1.594 (13)	O(12)—P(11)—O(13)	114.0 (5)
P(12)—O(15)	1.504 (9)	O(12)—P(11)—O(14)	113.4 (5)
P(12)—O(16)	1.526 (11)	O(13)—P(11)—O(14)	110.5 (6)
P(12)—O(17)	1.464 (10)	O(11)—P(12)—O(15)	108.1 (7)
		O(11)—P(12)—O(16)	108.6 (7)
		O(11)—P(12)—O(17)	103.3 (6)
		O(15)—P(12)—O(16)	112.1 (6)
		O(15)—P(12)—O(17)	111.6 (7)
		O(16)—P(12)—O(17)	112.4 (7)
P(21)—O(21)	1.664 (14)	P(21)—O(21)—P(22)	130.3 (13)
P(21)—O(22)	1.405 (20)	O(21)—P(21)—O(22)	110.6 (11)
P(21)—O(23)	1.514 (19)	O(21)—P(21)—O(23)	96.9 (8)
P(21)—O(24)	1.491 (19)	O(21)—P(21)—O(24)	99.6 (8)
P(22)—O(21)	1.571 (23)	O(22)—P(21)—O(23)	116.0 (10)
P(22)—O(25)	1.529 (18)	O(23)—P(21)—O(24)	113.3 (13)
P(22)—O(26)	1.498 (18)	O(22)—P(21)—O(24)	116.6 (10)
P(22)—O(27)	1.595 (15)	O(21)—P(22)—O(25)	112.5 (9)
		O(21)—P(22)—O(26)	114.1 (10)
		O(21)—P(22)—O(27)	103.2 (10)
		O(25)—P(22)—O(26)	113.9 (12)
		O(25)—P(22)—O(27)	106.2 (8)
		O(26)—P(22)—O(27)	105.5 (8)
P(21)—O(211)	1.58 (6)	P(21)—O(211)—P(22)	130.0 (3)
P(21)—O(221)	1.69 (2)	O(211)—P(21)—P(221)	104.9 (22)
P(22)—O(211)	1.65 (4)		
P(22)—O(271)	1.29 (4)	O(211)—P(22)—O(271)	109.6 (28)
O(82)—O(83)	1.402 (16)		
O(84)—O(85)	1.45 (2)		
C(1)—N(11)	1.32 (2)	N(11)—C(1)—N(12)	120.0 (15)
C(1)—N(12)	1.34 (2)	N(11)—C(1)—N(13)	121.2 (14)
C(1)—N(13)	1.30 (2)	N(12)—C(1)—N(13)	118.6 (14)
C(2)—N(21)	1.40 (3)	N(21)—C(2)—N(22)	119.2 (21)
C(2)—N(22)	1.28 (1)	N(21)—C(2)—N(23)	116.5 (14)
C(2)—N(23)	1.32 (3)	N(22)—C(2)—N(23)	124.2 (22)
C(3)—N(31)	1.38 (2)	N(31)—C(3)—N(32)	121.1 (18)
C(3)—N(32)	1.34 (4)	N(32)—C(3)—N(33)	122.1 (16)
C(3)—N(33)	1.36 (2)	N(31)—C(3)—N(33)	116.6 (26)
C(4)—N(41)	1.32 (4)	N(41)—C(4)—N(42)	122.3 (20)
C(4)—N(42)	1.36 (2)	N(41)—C(4)—N(43)	122.4 (17)
C(4)—N(43)	1.39 (2)	N(42)—C(4)—N(43)	114.8 (23)
C(5)—N(51)	1.32 (3)	N(51)—C(5)—N(52)	119.3 (13)
C(5)—N(52)	1.39 (3)	N(51)—C(5)—N(53)	122.3 (21)
C(5)—N(53)	1.29 (1)	N(52)—C(5)—N(53)	118.2 (19)
C(6)—N(61)	1.32 (1)	N(61)—C(6)—N(62)	119.2 (20)
C(6)—N(62)	1.34 (2)	N(61)—C(6)—N(63)	122.8 (20)
C(6)—N(63)	1.34 (3)	N(62)—C(6)—N(63)	117.9 (13)
C(7)—N(71)	1.33 (1)	N(71)—C(7)—N(72)	120.1 (19)
C(7)—N(72)	1.34 (3)	N(71)—C(7)—N(73)	118.8 (21)
C(7)—N(73)	1.30 (2)	N(72)—C(7)—N(73)	120.9 (14)
C(8)—N(81)	1.30 (2)	N(81)—C(8)—N(82)	118.5 (14)
C(8)—N(82)	1.34 (2)	N(81)—C(8)—N(83)	119.9 (14)
C(8)—N(83)	1.34 (2)	N(82)—C(8)—N(83)	120.9 (18)

The orientational disorder does not affect the chain formation since the particular O atoms involved are very close in position whichever orientation is adopted.

This pyrophosphate group is staggered as in the related hydrate (Adams & Ramdas, 1977) and PYR1: this is not always the case for pyrophosphates [e.g. Leung & Calvo (1972) found for $\text{Na}_4\text{P}_2\text{O}_7$, a partly eclipsed conformation]. The bond lengths and angles in the

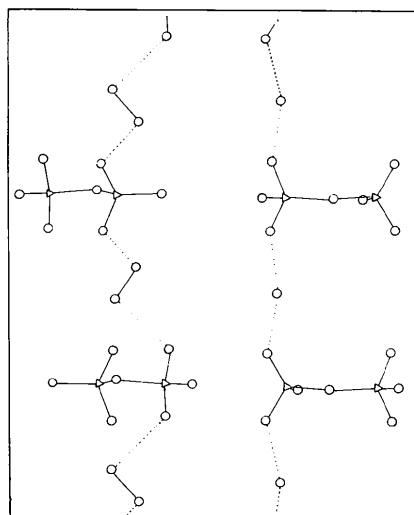


Fig. 3. Projections of the pyrophosphate chains on to (001).

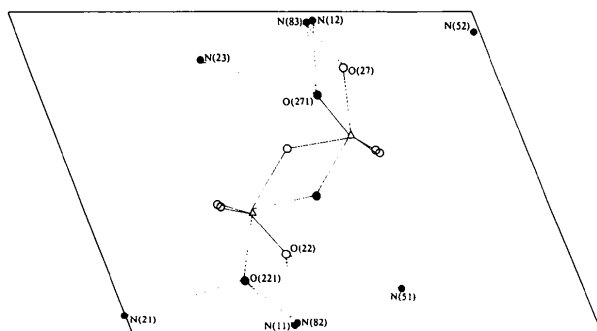


Fig. 4. The two orientations of the pyrophosphate PYR2.

inverted orientation of PYR2 are rather poorly determined. There appear to be no abnormally short contacts caused by the disorder of the PYR2 molecules. The N atoms forming hydrogen bonds to O atoms of this group form alternative hydrogen bonds with slightly altered parameters (Table 4).

The guanidinium groups form hydrogen bonds (Fig. 5) which hold the $(\cdots P_2O_7 \cdots H_2O \cdots)_n$ and $(\cdots P_2O_7 \cdots H_2O_2 \cdots)_n$ chains together. All the H atoms of these cations are used in hydrogen bonding except that N(63) and N(72) each form only one such bond. The bonds from N(21) \cdots O(82) and N(52) \cdots O(84) are also quite long. In this perhydrate there is one hydrogen bond from a guanidinium ion to the bridge O(11). This feature is not seen in trisguanidinium hydrogen pyrophosphate (Adams & Ramdas, 1976) but does occur in guanidinium pyrophosphate monohydrate (Adams & Ramdas, 1977). This may be due to the overall negative charge residing

Table 4. *Hydrogen-bonding geometry*

E.s.d.'s for hydrogen-bond lengths are 0.02–0.03 Å. Bonds enclosed in { } brackets are the bonds formed to whichever inverted pyrophosphate is present.

N(11) \cdots O(13)	2.92 Å	[N(52) \cdots O(84)	3.30 Å
{N(11) \cdots O(22 ^b)	2.99}	N(53) \cdots O(26 ^{vi})	2.84
N(11) \cdots O(221 ^b)	2.92	N(53) \cdots O(25 ⁱ)	2.96
N(12) \cdots O(14)	2.92	N(61) \cdots O(81)	2.76
{N(12) \cdots O(27 ⁱⁱ)	2.85}	N(61) \cdots O(25 ^{vi})	2.81
{N(12) \cdots O(271 ⁱⁱ)	2.93}	N(62) \cdots O(81)	3.04
N(13) \cdots O(24 ^b)	2.82	N(62) \cdots O(11)	3.10
N(13) \cdots O(25 ⁱⁱ)	2.87	N(63) \cdots O(17)	2.89
N(21) \cdots O(221 ⁱⁱⁱ)	3.13	N(71) \cdots O(86)	2.79
[N(21) \cdots O(82)	3.27]	N(71) \cdots O(23 ⁱⁱⁱ)	2.89
N(22) \cdots O(24 ⁱⁱⁱ)	2.82	N(72) \cdots O(12 ^v)	3.00
N(22) \cdots O(23 ⁱⁱ)	2.95	N(73) \cdots O(86)	3.24
N(23) \cdots O(82)	2.89	N(73) \cdots O(16 ^v)	3.04
{N(23) \cdots O(27 ^{iv})	3.12}	N(81) \cdots O(23 ^v)	2.82
N(23) \cdots O(271 ^{iv})	3.13]	N(81) \cdots O(26 ^{vii})	2.83
N(31) \cdots O(14 ^{iv})	2.82	{N(82) \cdots O(22 ^v)	2.87}
N(31) \cdots O(17)	2.84	N(82) \cdots O(221 ^v)	2.79}
N(32) \cdots O(16 ^b)	2.89	N(82) \cdots O(87 ^{viii})	2.97
N(32) \cdots O(84)	3.02	{N(83) \cdots O(27 ^{vii})	2.89}
N(33) \cdots O(12 ^b)	2.86	N(83) \cdots O(271 ^{vii})	3.03}
N(33) \cdots O(87 ^b)	3.11	N(83) \cdots O(83)	3.16
N(41) \cdots O(15 ^v)	2.77	O(81) \cdots O(23 ^{vii})	2.82
N(41) \cdots O(82)	3.14	O(81) \cdots O(26 ⁱ)	2.83
N(42) \cdots O(13 ^{iv})	2.80	O(86) \cdots O(24 ^{vii})	2.90
N(42) \cdots O(17)	2.81	O(86) \cdots O(25 ^v)	2.84
N(43) \cdots O(12 ^v)	2.89	O(87) \cdots O(12)	2.82
N(43) \cdots O(85 ^{iv})	3.11	O(87) \cdots O(17 ^{ix})	2.99
N(51) \cdots O(84)	2.94	O(82) \cdots O(14)	2.57
N(51) \cdots O(22 ⁱ)	3.00	O(83) \cdots O(15 ^v)	2.65
N(52) \cdots O(27 ^{vi})	3.05	O(84) \cdots O(13)	2.60
		O(85) \cdots O(16 ⁱ)	2.66

Symmetry operations

- | | |
|--|--|
| (i) $\frac{1}{2} - x, -\frac{1}{2} + y, 1 - z$ | (vi) $-\frac{1}{2} + x, \frac{1}{2} - y, -1 + z$ |
| (ii) $x, y, -1 + z$ | (vii) $x, y, -1 + z$ |
| (iii) $-x, 1 - y, 1 - z$ | (viii) $1 - x, 1 - y, 1 - z$ |
| (iv) $-\frac{1}{2} + x, \frac{1}{2} - y, z$ | (ix) $\frac{1}{2} + x, \frac{1}{2} - y, z$ |
| (v) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$ | |

on the anion. The water molecules O(81), O(86) and O(87) all donate two hydrogen bonds to pyrophosphate O atoms and accept two hydrogen bonds from guanidinium ions (Fig. 6). O(87) has two other close contacts with O atoms of the H_2O_2 molecules, *i.e.* O(83) 3.11, O(85) 2.99 Å.

The bond lengths of the H_2O_2 molecules (~ 1.4 Å) are shorter than the ideal value of 1.49 Å, but this effect has often been noted before (Pedersen, 1972) and ascribed to thermal motion or even to a small degree of random substitution of H_2O_2 by H_2O . The hydrogen bonds formed by these molecules are rather short at ~ 2.6 Å, but are comparable with such bonds formed in other perhydrates (*e.g.* Adams & Pritchard, 1976). The hydrogen bonding involving H_2O_2 is stronger than that for comparable hydrates. It might be supposed that perhydrates are of greater stability than related

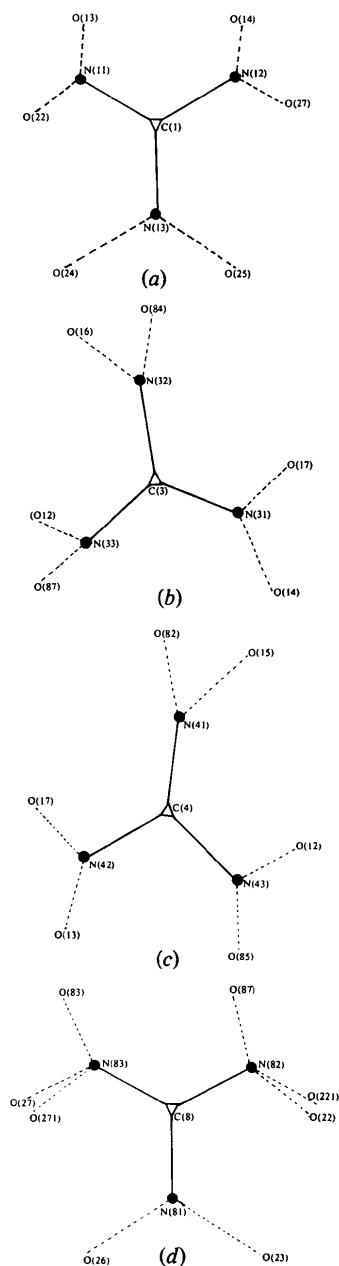


Fig. 5. Projections of some of the guanidinium ions showing their hydrogen bonding; (a) C(1) on to (100), (b) C(3) on to (001), (c) C(4) on to (001), (d) C(8) on to (100).

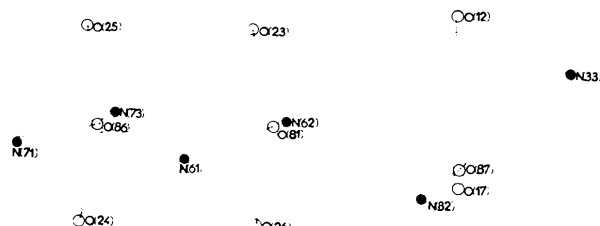


Fig. 6. The hydrogen-bonding environments around the water molecules O(81), O(86) and O(87).

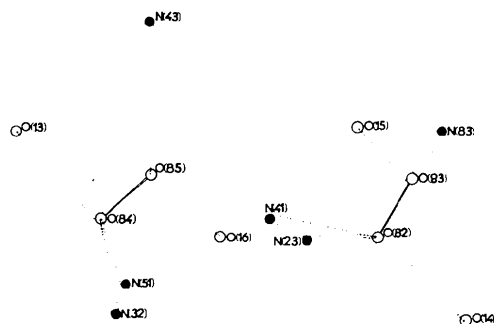


Fig. 7. The hydrogen-bonding schemes of the H_2O_2 molecules O(82), O(83) and O(84), O(85).

hydrates. This is not found to be the case. One reason for this is that the solid hydrate is stabilized by the pressure of the H_2O vapour in the atmosphere whereas no similar H_2O_2 vapour exists. The H_2O_2 molecules here are somewhat unusual in that they accept three hydrogen bonds from guanidinium cations (Fig. 7). In the more usual case (*e.g.* oxalate perhydrates, Pedersen, 1969) the H_2O_2 species accept only two such bonds. It has been suggested (Pedersen, 1969) that the great stability of the urea–hydrogen peroxide adduct (Lu, Hughes & Giguère, 1941) might arise because this is the only known perhydrate in which H_2O_2 donates two hydrogen bonds and also accepts four.

If we assume that the H atoms of the H_2O_2 molecules lie along the hydrogen-bond direction then the dihedral angle calculated is 129° for the O(82), O(83) and 138° for the O(84), O(85) molecule. This compares with a gas-phase value of 115° (Hunt, Leacock, Peters & Hecht, 1965).

It is instructive to compare this perhydrate with guanidinium pyrophosphate monohydrate and the series of perhydrates formed by alkali-metal oxalates (Pedersen, 1969). In the first we have infinite chains of $(\dots\text{P}_2\text{O}_7\cdots\text{H}_2\text{O}\cdots)_n$ running through the structure; the repeat distance between these chains is given by the a axis length of 7.05 \AA . In crystals of the title compound, on the other hand, we have in every alternate chain the water molecules replaced by H_2O_2 ; the corresponding axis length here is 14.15 \AA (b axis) which is double the value for the hydrate. Other relatively stable pyrophosphate perhydrates exist with formulae such as $\text{Na}_3\text{HP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}_2$ (Wado, Nakatani & Sato, 1971) and $\text{K}_4\text{P}_2\text{O}_7 \cdot x\text{H}_2\text{O}_2$ (Majewski, 1970). It may be that there is a common structural feature [*i.e.* chains of $(\dots\text{P}_2\text{O}_7\cdots\text{H}_2\text{O}_2\cdots)_n$] in each of these structures. However, since the ratio of H_2O_2 to pyrophosphate anions is greater than one, it implies that if such chains exist there must be extra H_2O_2 molecules packed into the structure in other ways, *e.g.* hydrogen

Table 5. Deviations of atoms from least-squares planes (Å)

(1) Plane through C(1), N(11), N(12), N(13) 15.9353x - 0.7097y - 0.0598z = 5.4171				(4) Plane through C(4), N(41), N(42), N(43) -2.1130x + 0.2427y + 16.6484z = 6.9307				(7) Plane through C(7), N(71), N(72), N(73) -5.5366x + 13.1689y - 0.5982z = 8.7148			
C(1)	-0.009	N(12)	0.003	C(4)	0.032	N(42)	-0.010	C(7)	0.007	N(72)	-0.003
N(11)	0.003	N(13)	0.003	N(41)	-0.012	N(43)	-0.010	N(71)	-0.002	N(73)	-0.003
(2) Plane through C(2), N(21), N(22), N(23) -1.8708x + 13.7802y - 2.3597z = 5.6666				(5) Plane through C(5), N(51), N(52), N(53) -1.2430x + 13.7693y - 2.9270z = -1.2350				(8) Plane through C(8), N(81), N(82), N(83) 15.6843x - 0.0295y + 0.5223z = 5.5460			
C(2)	0.003	N(22)	-0.001	C(5)	-0.003	N(52)	0.001	C(8)	0.043	N(82)	-0.014
N(21)	-0.001	N(23)	-0.001	N(51)	0.001	N(53)	0.001	N(81)	-0.014	N(83)	-0.014
(3) Plane through C(3), N(31), N(32), N(33) -2.3006x - 1.4067y + 16.6350z = 6.8387				(6) Plane through C(6), N(61), N(62), N(63) -5.3835x + 13.3292y + 0.0704z = 2.2752							
C(3)	-0.010	N(32)	0.001	C(6)	-0.007	N(62)	0.002				
N(31)	0.003	N(33)	0.003	N(61)	0.002	N(63)	0.002				

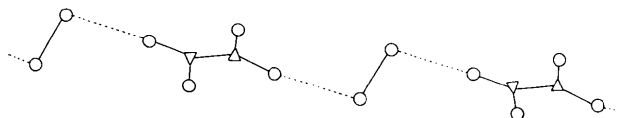


Fig. 8. Projection of the structure of potassium oxalate perhydrate showing the hydrogen-bonded chains of, alternately, $C_2O_4^{2-}$ and H_2O_2 .

bonding the chains together. In the series of oxalate perhydrates studied by Pedersen there exist similar infinite chains of $(\cdots C_2O_4 \cdots H_2O_2 \cdots)_n$ (Fig. 8) although the manner of packing these together varies with the cation used as, indeed, does the chemical stability of the solids formed.

Deviations of atoms from the least-squares planes are shown in Table 5.

The structural similarity between guanidinium pyrophosphate monohydrate and the title compound (in the former, half the structural chains have H_2O_2 substituted by H_2O) suggested that it might be possible to replace more of the H_2O by H_2O_2 . We have now crystallized a new phase from a solution of guanidinium pyrophosphate in 85% (w/w) H_2O_2 solution. This structure will be investigated in the near future.

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