

The Crystal Structure of Guanidinium Oxalate Dihydrate Monoperhydrate

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The structure of $[\text{C}(\text{NH}_2)_3]_2(\text{COO})_2 \cdot 2\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$ has been determined from microdensitometer-measured intensities and refined to a final R of 0.061. The geometrical parameters of the ions and molecules are normal with the oxalate ions and H_2O_2 molecules disposed across centres of symmetry; both these species are planar. Although the perhydrates of all the alkali metal (and ammonium) oxalates have hydrogen-bonded chains of $(\cdots\text{oxalate}\cdots\text{H}_2\text{O}_2\cdots)_n$, these are not a feature of the title compound which has a three-dimensional hydrogen-bonding scheme involving eight of the nine H atoms. This compound is much more stable than other oxalate perhydrates.

Introduction

Perhydrates, *i.e.* substances containing H_2O_2 of crystallization, have been grown from a few organic compounds, notably urea (Lu, Hughes & Giguère, 1941) and alkali metal oxalates (Pedersen, 1969). However, these have not been very stable and, in general, undergo decomposition at room temperature over a period of days. The structures of the oxalate hydrates and perhydrates have been shown by Pedersen (1969) to consist of chains (Fig. 1) which are linked in the ammonium salt by hydrogen bonds. We have taken this opportunity to maximize the number of possible hydrogen bonds by using the guanidinium ion $[\text{C}(\text{NH}_2)_3]^+$ as a method of increasing the stability of the perhydrate. The relative stabilities of ammonium oxalate perhydrate and the title compound are indicated by the time taken for a 20% fall in 'activity', approximately 50 h for the former and 250 h for the latter.

Experimental

Guanidinium oxalate was prepared by reaction of guanidinium carbonate with the acid; the salt was recrystallized at room temperature from 30% (w/v) hydrogen peroxide. Analysis of the crystals for H_2O_2 was carried out by $\text{I}_2/\text{S}_2\text{O}_3^{2-}$ titrations and the stability studies were at room temperature and humidity (approximately 50%). Two different crystals (both about $0.7 \times 0.7 \times 0.7$ mm) were used to collect the two data sets ($hk0$ – $hk3$, $h0l$ – $h3l$) on a Stoe–Weissenberg camera. The crystal data are given in Table 1. The intensities were measured by the SRC Microdensitometer Service at the Atlas Computer Laboratory with an Optronics P1000 scanner.

Table 1. Crystal data

Space group $P2_1/c$; $a=6.96$ (3), $b=9.46$ (3), $c=10.13$ (3) Å
 $\beta=114.0$ (1)°; (Cu $K\alpha$, $\lambda=1.5418$ Å); $Z=2$
 $d_m=1.472$, $d_c=1.458$ g cm $^{-3}$

Determination of the structure

Intensities were measured for 1333 reflexions, of which 585 were unique. The planes which were too weak to be measured by the scanner were given intensities equal to half the weakest observed value on the appropriate film pack, and the data were corrected for Lorentz and polarization effects. A Wilson plot gave the low B of 1.0 Å 2 , and E values were generated.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1970) with the 119 planes with $E > 1.4$. An E map computed with the phases from the set with the highest figure of merit (1.20) revealed a chemically reasonable set of peaks.

Refinement was by anisotropic full-matrix least squares; the H atoms were found from a difference synthesis when R was 0.08. During further refinement the thermal parameters of the H atoms were constrained to be equal to the mean value of $(U_{11} + U_{22} + U_{33})$ for the heavy atoms. In the last cycle the shifts were of the order of the appropriate standard deviations; the final R was 0.061. The scattering factors were those listed in *International Tables for X-ray Crystallography* (1962) and all calculations, except the structure solution, were made with the X-RAY system (1972).

Final atomic and thermal parameters are given in Tables 2 and 3.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31732 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

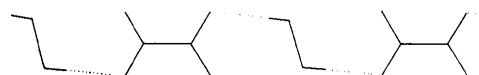


Fig. 1. Schematic diagram of hydrogen bonding in other oxalate perhydrate structures.

Table 2. Fractional atomic coordinates and their standard deviations

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	0.2325 (7)	0.2580 (5)	0.1120 (5)
O(2)	0.5932 (7)	0.0751 (5)	0.1726 (5)
O(3)	0.6102 (6)	0.8522 (4)	0.1074 (5)
O(4)	0.9403 (7)	0.0563 (5)	0.0163 (5)
C(1)	0.5567 (8)	0.9794 (7)	0.0796 (6)
C(2)	0.7853 (8)	0.4205 (7)	0.1007 (7)
N(1)	0.6684 (8)	0.3825 (6)	-0.0330 (6)
N(2)	0.7947 (9)	0.3390 (7)	0.2097 (6)
N(3)	0.8920 (10)	0.5407 (6)	0.1259 (6)
H(1)	0.38 (1)	0.210 (8)	0.103 (8)
H(2)	0.25 (1)	0.299 (9)	0.179 (9)
H(3)	0.06 (1)	0.124 (8)	0.071 (7)
H(4)	0.85 (1)	0.594 (9)	0.071 (9)
H(5)	1.00 (1)	0.543 (9)	0.218 (9)
H(6)	0.88 (1)	0.369 (9)	0.292 (9)
H(7)	0.71 (1)	0.260 (9)	0.188 (9)
H(8)	0.58 (1)	0.315 (8)	-0.058 (9)
H(9)	0.70 (1)	0.436 (9)	-0.105 (8)

Table 3. Temperature factors ($U_{ij} \times 10^3$) for the heavy atoms

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	39 (2)	26 (3)	30 (2)	-2 (2)	14 (2)	-12 (3)
O(2)	56 (3)	21 (2)	22 (2)	-3 (2)	12 (2)	-8 (3)
O(3)	38 (2)	16 (2)	27 (3)	3 (2)	6 (2)	6 (3)
O(4)	39 (2)	39 (3)	47 (3)	-7 (2)	18 (2)	-2 (3)
C(1)	24 (3)	18 (3)	22 (3)	-1 (2)	6 (2)	11 (4)
C(2)	23 (3)	25 (3)	23 (3)	-9 (3)	4 (2)	-1 (4)
N(1)	39 (3)	29 (3)	20 (3)	-14 (3)	6 (2)	-5 (4)
N(2)	55 (4)	36 (4)	20 (3)	-17 (3)	8 (3)	6 (4)
N(3)	47 (3)	31 (3)	28 (3)	-17 (3)	7 (3)	-8 (4)

Description and discussion of the structure

Bond lengths and angles (Table 4) in the oxalate ion are similar to those previously found (Pedersen, 1969) although the C-C bond is closer to the theoretical single-bond length of 1.54 Å than to the lengthened value sometimes observed (Hodgson & Ibers, 1969) of up to 1.57 Å. The guanidinium ion parameters are likewise close to those usually found with all the C-N bonds of equal length (Adams & Small, 1976), thus contrasting with guanidinium carbonate where one of

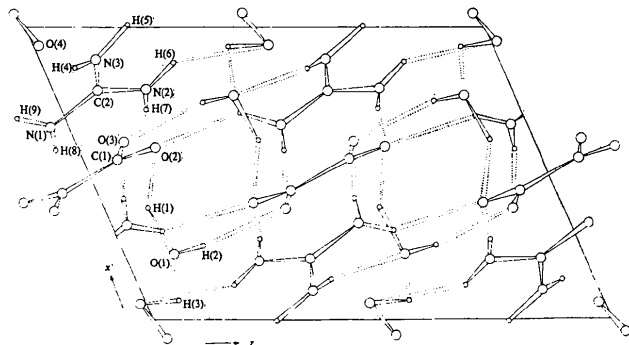


Fig. 2. View of the structure projected down the *b* axis. The hydrogen-bonding scheme is shown.

Table 4. Bond lengths and angles

O(4)-O(4')	1.468 (9) Å	C(1)-C(1')-O(2)	117.9 (6)°
C(1)-C(1')	1.530 (10)	C(1)-C(1')-O(3)	117.3 (6)
C(1)-O(2)	1.255 (9)	O(2)-C(1)-O(3)	124.8 (6)
C(1)-O(3)	1.257 (9)	N(1)-C(2)-N(2)	119.9 (6)
C(2)-N(1)	1.315 (9)	N(1)-C(2)-N(3)	119.8 (7)
C(2)-N(2)	1.327 (10)	N(2)-C(2)-N(3)	120.3 (6)
C(2)-N(3)	1.325 (10)	O(4)-O(4')-H(3)	98.8 (4.6)
O(1)-H(1)	1.18 (9)	H(2)-O(3)-H(1)	115 (7)
O(1)-H(2)	0.74 (9)	H(8)-N(1)-C(2)	125 (6)
O(4)-H(3)	1.03 (7)	H(8)-N(1)-H(9)	121 (7)
N(1)-H(8)	0.87 (8)	H(9)-N(1)-C(2)	113 (4)
N(1)-H(9)	0.98 (9)	H(6)-N(2)-C(2)	113 (6)
N(2)-H(6)	0.85 (7)	H(6)-N(2)-H(7)	130 (8)
N(2)-H(7)	0.90 (8)	H(7)-N(2)-C(2)	117 (5)
N(3)-H(4)	0.72 (9)	H(4)-N(3)-C(2)	117 (6)
N(3)-H(5)	0.94 (7)	H(4)-N(3)-H(5)	131 (8)
		H(5)-N(3)-C(2)	112 (5)

these bonds is significantly longer than the other two (Adams & Small, 1974).

The O-O distance in the H_2O_2 molecule is similar to those in other perhydrates and peroxy compounds (Pedersen, 1972) and the HOO angle is close to that found by Busing & Levy (1965) in solid H_2O_2 (102.7°) although the e.s.d. is very large. The dihedral angle between the two H-O bonds is 180° since the molecule is planar (Table 5); dihedral angles between 90° and 180° have been found in other perhydrates, the value apparently being very sensitive to the environment of the H_2O_2 molecules.

Table 5. Least-squares planes and deviations of atoms from them (Å)

(a) Plane through the oxalate ion - defined by all six atoms

$$5.0251x + 1.3460y - 3.2912z = 3.8585$$

C(1)	-0.005	O(2)	0.001	O(3)	0.001
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(b) Plane through the guanidinium ion - defined by C(2), N(1), N(2), N(3)

$$4.7043x - 3.5508y - 3.0845z = 1.8886$$

C(2)	0.002	H(4)	-0.282	H(8)	-0.100
N(1)	-0.001	H(5)	0.215	H(9)	0.180
N(2)	-0.001	H(6)	0.040		
N(3)	-0.001	H(7)	-0.052		

(c) Plane through the hydrogen peroxide molecule - defined by all four atoms

$$-0.5870x - 3.0473y + 8.3786z = 0.0$$

There is a major difference between the title compound and all other oxalate perhydrates in that none has previously been reported which contains water together with the hydrogen peroxide of crystallization. The hydrogen-bonding scheme is the same in all these other perhydrates; there are infinite chains of type $(\dots \text{oxalate} \dots H_2O_2 \dots)_n$ with the cations situated between them, whereas this structural feature is not present in the guanidinium salt where there is a complicated three-dimensional hydrogen-bonding network (Figs. 2 and 3, Table 6).

Table 6. *Hydrogen-bonding geometry*

Bonds (<i>a</i> - <i>b</i> ... <i>c</i>)	Distances (Å)		Angles (°)
	<i>bc</i>	<i>ac</i>	<i>abc</i>
O(4)-H(3)···O(1 ⁱ)	1.66 (7)	2.67 (1)	163 (7)
O(1)-H(1)···O(2)	1.85 (7)	2.90 (1)	146 (7)
O(1)-H(2)···O(3 ⁱⁱ)	2.04 (8)	2.75 (1)	159 (8)
N(1)-H(8)···O(3 ⁱⁱⁱ)	1.97 (8)	2.84 (1)	174 (7)
N(1)-H(9)···O(2 ^{iv})	2.07 (8)	2.84 (1)	134 (6)
N(2)-H(6)···O(4 ^v)	2.25 (9)	3.02 (1)	149 (9)
N(2)-H(7)···O(2)	1.92 (9)	2.81 (1)	168 (6)
N(3)-H(4)···O(1 ^{vi})	2.20 (9)	2.91 (1)	172 (11)

Equivalent positions

(i)	1+x	y	z	(ii)	1-x	-½+y	½-z
(iii)	-x	1-y	1-z	(iv)	-1+x	½-y	½+z
(v)	x	½-y	½+z	(vi)	1-x	1-y	-z

The peroxide O(4) forms a hydrogen bond (2.69 Å) to the water O(1), which also accepts a hydrogen bond (2.92 Å) from one of the guanidinium groups. The water molecule donates two hydrogen bonds (2.75 and 2.91 Å) to different oxalate anions. The guanidinium ion also provides a hydrogen bond (3.01 Å) to the peroxide O and three other hydrogen bonds (2.81, 2.83 and 2.85 Å) to oxalate ions. This hydrogen-bonding scheme uses eight of the nine possible H atoms.

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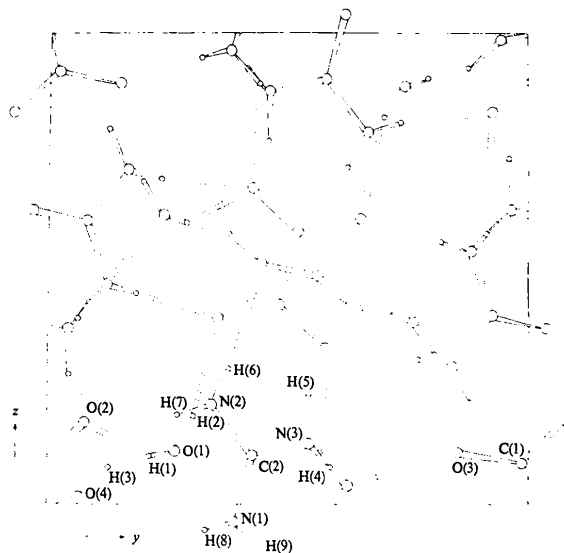


Fig. 3. View of the structure projected down the *a* axis. The hydrogen-bonding scheme is shown.

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Structure Cristalline du Polyphosphate de Lithium-Ammonium, $\text{Li}_2\text{NH}_4(\text{PO}_3)_3$

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Lithium ammonium polyphosphate, $\text{Li}_2\text{NH}_4(\text{PO}_3)_3$, is orthorhombic, *Pbca*, with a unit cell $a = 12.199(5)$, $b = 13.047(5)$, $c = 10.537(5)$ Å and $Z = 8$. The crystal structure of this salt has been solved by using 2297 independent reflexions. The final *R* value is 0.043. PO_3 chains, with a period of six tetrahedra, run along the *b* direction. Associated cations, all in fourfold coordination, also form chains running along the *b* direction.

Introduction

Les cristaux du polyphosphate de lithium-ammonium, $\text{Li}_2\text{NH}_4(\text{PO}_3)_3$, se présentent sous la forme de plaquet-

tes épaisses à contours irréguliers. On les prépare facilement en calcinant à 350°C, durant une quinzaine d'heures, un mélange de 3 g de carbonate de lithium et de 20 g de phosphate biammonique. Les cristaux