

The Crystal Structure of Guanidinium Pyromellitate Triperhydrate

J. M. ADAMS and VIJAYALAKSHMI RAMDAS

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

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Perhydrates are solids which contain H_2O_2 of crystallisation in an analogous fashion to the water in crystalline hydrates. They are of considerable technological importance: the structures of some of the more stable perhydrates have been reported recently (e.g. $Na_2CO_3 \cdot 1.5H_2O_2$ [1] and $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ [2]). There do not appear, however, to have been many systematic studies of perhydrates excepting that of Pedersen [3] on the alkali metal oxalate monoperhydrates. Some time ago, in these laboratories, we attempted to bring together work on multiple hydrogen bond forming cations (e.g. the guanidinium ion [4]) and some studies of stable perhydrates. This has led to the discovery of several relatively stable perhydrates such as guanidinium pyrophosphate monoperhydrate sesquihydrate [5] and the presentation of the idea that it might be possible to design stable peroxide carriers by maximising the possibility of hydrogen bonding [6]. It has been found that guanidinium pyromellitate forms two distinct perhydrates; one is a trihydrate monoperhydrate [7], the other is the title compound.

Experimental

Colourless parallelepiped crystals were formed upon slow crystallisation of a solution of the di- or trihydrate in 50% (w/w) H_2O_2 . On exposure to the atmosphere the crystals became white and opaque. In acid Ti(IV) solution a characteristic orange precipitate formed which confirmed the presence in the crystals of H_2O_2 . A thermogravimetric analysis of the sample gave a weight loss of 17.2%, corresponding to the triperhydrate and confirming the iodimetric result (16.8%). The crystals then, are of a true perhydrate and do not contain any water of crystallisation in addition to the H_2O_2 . The temperature at which the hydrogen peroxide is lost is 55 °C, which is higher than that at which water is lost from the trihydrate (~ 30 °C) and dihydrate (~ 30 °C) – thus preserving a trend observed in other perhydrates and related hydrates. The perhydrate itself is relatively unstable – losing all of the H_2O_2 in a few days to give the anhydrous compound which does

not rehydrate under ambient conditions (typically 40–50% RH, 20 °C).

Crystal data are: Space Group $P\bar{1}$; $a = 8.19(5)$, $b = 7.926(3)$, $c = 12.51(5)$ Å, $\alpha = 96.8(1)$, $\beta = 110.2(1)$, $\gamma = 113.8(1)^\circ$. $d_{obs} = 1.47$ g cm⁻³, $d_{calc} = 1.45$ g cm⁻³; $\mu = 10.3$ cm⁻¹.

Two crystals (coated with varnish to protect them from atmospheric humidity) were used to collect the photographic data which were then microdensitometer scanned, corrected for absorption and put on a common scale [8].

The structure was solved using the direct methods program EES in SHELX76 [9]. One guanidinium group and one H_2O_2 molecule were located from a difference synthesis. The refinement (with anisotropic temperature factors) gave $R = 10\%$. A list of the observed and calculated structure factors can be obtained from the authors. The final atomic parameters are given in Table I.

TABLE I. Fractional Atomic Coordinates and their Standard Deviations.

	x	y	z
C(1)	1.082(2)	0.911(2)	1.077(1)
C(2)	1.017(2)	0.843(2)	0.954(1)
C(3)	0.935(2)	0.928(2)	0.874(1)
C(21)	1.040(2)	0.669(2)	0.905(1)
O(21)	0.925(1)	0.564(1)	0.807(1)
O(22)	1.185(1)	0.655(1)	0.974(1)
C(31)	0.863(2)	0.863(2)	0.742(1)
O(31)	0.990(2)	0.901(2)	0.701(1)
O(32)	0.679(1)	0.780(1)	0.681(1)
C(11)	0.587(2)	0.492(2)	0.166(1)
N(11)	0.562(2)	0.315(2)	0.171(1)
N(12)	0.502(2)	0.569(2)	0.223(1)
N(13)	0.708(2)	0.596(2)	0.127(1)
C(22)	0.751(3)	0.268(2)	0.539(1)
N(21)	0.669(2)	0.122(2)	0.432(1)
N(22)	0.909(2)	0.302(2)	0.626(1)
N(23)	0.649(2)	0.366(2)	0.544(1)
O(1)	0.503(2)	0.918(1)	1.174(1)
O(2)	0.360(2)	1.035(2)	0.873(1)
O(3)	0.903(2)	0.907(2)	0.479(1)
H(1)	1.162(6)	0.854(6)	1.134(1)

Results and Discussion

The geometry of the guanidinium cations and the pyromellitate anion (Table II) is consistent with that usually found (within the standard deviations of the parameters). The only unusual feature is that the angles of twist of the carboxyl groups and of the plane of the pyromellitate ring are here 21.3° and 64.9° compared with 15.9° and 84.5° in guanidinium pyromellitate trihydrate monoperhydrate [7] and 21.4° and 74.5° in the acid dihydrate [10]. These

TABLE II. Bond Lengths and Angles.

C(1)–H(1)	1.06(6) Å	H(1)–C(1)–C(2)	119(4)°
C(1)–C(2)	1.39(2)	C(2)–C(1)–C(3 ⁱ)	120(2)
C(1)–C(3 ⁱ)	1.42(2)	C(3)–C(2)–C(1)	122(2)
C(2)–C(3)	1.39(2)	C(1)–C(2)–C(21)	118(2)
C(21)–C(2)	1.55(3)	C(3)–C(2)–C(21)	119(2)
C(21)–O(21)	1.18(2)	C(2)–C(21)–O(21)	118(2)
C(21)–O(22)	1.26(3)	C(2)–C(21)–O(22)	116(2)
C(31)–C(3)	1.50(2)	O(21)–C(21)–O(22)	126(2)
C(31)–O(31)	1.26(2)	C(2)–C(3)–C(31)	125(2)
C(31)–O(32)	1.25(2)	C(1 ⁱ)–C(3)–C(31)	117(2)
C(11)–N(11)	1.34(3)	C(3)–C(31)–O(31)	118(2)
C(11)–N(12)	1.39(3)	C(3)–C(31)–O(32)	116(2)
C(11)–N(13)	1.29(3)	O(31)–C(31)–O(32)	126(2)
C(22)–N(21)	1.40(3)	N(11)–C(11)–N(12)	116(2)
C(22)–N(22)	1.26(3)	N(11)–C(11)–N(13)	121(2)
C(22)–N(23)	1.36(4)	N(12)–C(11)–N(13)	122(2)
O(1)–O(2 ⁱⁱ)	1.45(3)	N(21)–C(22)–N(22)	121(2)
O(3)–O(3 ⁱⁱⁱ)	1.50(2)	N(21)–C(22)–N(23)	116(2)
		N(22)–C(22)–N(23)	123(2)

Symmetry code:

- (i) $2 - x, 2 - y, 2 - z$
(ii) $1 - x, 2 - y, 2 - z$
(iii) $2 - x, 2 - y, 1 - z$
(iv) $x, -1 + y, -1 + z$
(v) $x, y, -1 + z$

angles are dependent upon the hydrogen bond formation since the energy of hydrogen bonding is comparable with that required to rotate the carboxyl group. The O–O bond distances in the hydrogen peroxide molecules are close to the usual single bond value of *ca.* 1.50 Å. The molecule O(3)–O(3ⁱⁱⁱ) is *trans* planar as a consequence of being disposed across a centre of symmetry – a feature found in two of the oxalate perhydrates of Pedersen [3] and also in guanidinium oxalate dihydrate monoperhydrate [11]. The other H₂O₂ molecule (O(1)–O(2ⁱⁱ)) has a dihedral angle of *ca.* 154° (Fig. 2) compared with values ranging from 100° to 180° in other perhydrates. There is indeed, very little hindrance to the rotation of the H₂O₂ about its central single bond. In the free molecule the energy difference upon complete rotation is only 4 kJ mol⁻¹ [12].

It may be noted here that there is some evidence from the final electron density map for partial substitution of the H₂O₂ molecules by H₂O. This effect has been noted before in studies of perhydrates, especially by Pedersen [3].

The hydrogen bonding scheme (Figs. 1 and 2) is complicated, especially around the hydrogen peroxide groups. Every hydrogen atom of the guanidinium ions is involved in a hydrogen bond, with lengths ranging from 2.81–3.16 Å. There are four other reasonably close contacts involving the guanidinium nitrogen atoms: N(11)···O(1) at $x, -1 + y, -1 + z$, 3.02 Å; N(11)···O(32) at $1 - x, 1 - y, 1 - z$, 3.11 Å; N(12)···O(21) at $1 - x, 1 - y, 1 - z$, 3.05 Å; N(21)···O(32) at $1 - x, 1 - y, 1 - z$, 3.15 Å. Where there was some doubt about hydrogen bond

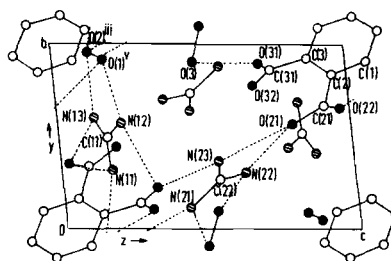
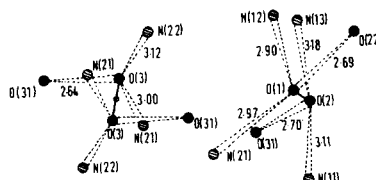
Fig. 1. Projection of the structure along the *a* axis.

Fig. 2. Hydrogen bonding arrangement around the hydrogen peroxide groups (distances in Å).

connectivity with bonds of comparable length the bond chosen was that which gave the most linear hydrogen bond (for this purpose the guanidinium hydrogen atoms were computed from regular geometry).

Pedersen [3] has suggested that the stability of perhydrates could be related to the number of hydrogen bonds donated to the H₂O₂ molecules in the structure. Urea perhydrate for example, is a very stable perhydrate in which the peroxide molecules accept the maximum of four hydrogen bonds [13]. Most other perhydrates accept only two hydrogen bonds although occasionally three are accepted [5]. However, in this case each H₂O₂ accepts four such bonds but the perhydrate itself is not exceptionally stable. Other factors must therefore also be of importance.

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References

- 1 J. M. Adams and R. G. Pritchard, *Acta Cryst.*, **B33**, 3650 (1977); M. A. A. F. de C. T. Carrondo, W. P. Griffith, D. P. Jones and A. C. Skapski, *J. Chem. Soc. Dalton*, 2323 (1977).
- 2 J. M. Adams, R. G. Pritchard and J. M. Thomas, *Chem. Comm.*, 228 (1978).
- 3 B. F. Pedersen, 'Structural Aspects of Perhydrates', Universitetsforlaget, Oslo (1969).
- 4 J. M. Adams and R. W. H. Small, *Acta Cryst.*, **B30**, 2191 (1974).

- 5 J. M. Adams and V. Ramdas, *Acta Cryst.*, *B34*, 2150 (1978).
- 6 J. M. Adams, R. G. Pritchard and J. M. Thomas, *Chem. Comm.*, 358 (1976).
- 7 J. M. Adams and V. Ramdas, *Acta Cryst.*, *B34*, 2781 (1978).
- 8 A. D. Rae and A. B. Blake, *Acta Cryst.*, *20*, 586 (1966).
- 9 G. M. Sheldrick, available on the Manchester CDC 7600 Regional Computer.
- 10 F. Takusagawa, K. Hirotsu and A. Shimada, *Bull. Chem. Soc. Jap.*, *44*, 1274 (1971).
- 11 J. M. Adams and R. G. Pritchard, *Acta Cryst.*, *B32*, 2432 (1976).
- 12 R. H. Hunt, A. Lencock, C. W. Peters and K. T. Hecht, *J. Chem. Phys.*, *42*, 1931 (1965).
- 13 C. S. Lu, E. W. Hughes and P. A. Giguere, *J. Am. Chem. Soc.*, *63*, 1507 (1941).