

For S—S, the present values bracket the mean of 2.029 Å ( $\sigma = 0.015$  Å). We have collected values for the C—S—S—C torsion angle for 72 occurrences in the Cambridge Structural Database (Allen *et al.*, 1979) (all having C—S—S—C in a non-cyclic system with  $R \leq 0.075$ ). The values cover a wide range (50–119°) and our results [82.4 (4)° (1) and 95.7 (4)° (2)] lie relatively close to the mean of 87° ( $\sigma = 13^\circ$ ).

We thank SERC and AERE Harwell for support under the CASE scheme.

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*Acta Cryst.* (1990). C46, 21–23

## Neutron Diffraction Study of Potassium Oxalate Monoperhydrate at 123 K\*

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(Received 16 August 1988; accepted 9 March 1989)

**Abstract.**  $K_2C_2O_4 \cdot H_2O_2$ ,  $M_r = 200.24$ , monoclinic,  $C2/c$ ,  $a = 8.858$  (2),  $b = 6.505$  (2),  $c = 10.872$  (2) Å,  $\beta = 108.38$  (1)°,  $V = 594.57$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.23$ ,  $D_m = 2.18$  g cm<sup>-3</sup>,  $\lambda = 1.0559$  (2) Å,  $\mu = 0.348$  cm<sup>-1</sup>,  $F(000) = 400$ ,  $T = 123.0$  (2) K,  $R = 0.0251$  for 2196 unique reflections. The hydrogen peroxide molecule has a skew conformation, the H—O—O—H torsion angle being 101.6°; O—O = 1.4578 (4), O—H = 1.0117 (5) Å, and O—O—H = 100.69 (3)°. The oxalate ion is centrosymmetric and planar; the two C—O distances are 1.2635 (3) and 1.2460 (3) Å, differing by 0.0175 Å, the longer one being the hydrogen-bond acceptor. The C—C distance is long, 1.5675 (5) Å.

**Introduction.** The structure of the title compound  $K_2C_2O_4 \cdot H_2O_2$  has been determined from film intensity data by Pedersen (1967). We are now determin-

ing the deformation electron density of the hydrogen peroxide molecule in different conformations to look for possible differences. We therefore have refined the X-ray crystal structure of the title compound at 123 K as well as the structure based on neutron diffraction data. The single-crystal neutron diffraction study was also inspired by the publication of neutron diffraction powder data for the deuterated compound apparently in error, as the authors claim the O—O distance of the hydrogen peroxide molecule to be 1.355 (8) Å (Adams, Ramdas & Hewat, 1980), compared to the old film-data value of 1.441 (9) Å (Pedersen, 1967). The neutron diffraction study is reported here.

**Experimental.** Potassium oxalate (p.a. Merck) was dissolved in perhydrol (30% H<sub>2</sub>O<sub>2</sub>). Crystals of  $K_2C_2O_4 \cdot H_2O_2$  were formed by slow evaporation. The crystals had a diamond-like form with the longest direction along a diagonal in the crystal lattice. The density was measured at room temperature by the flotation method. The crystals were grown in Norway and transported to the BNL High Flux Beam Reactor, USA. The dimensions of the

\* Part of this work was performed at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the US Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

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diagonals of the diamond-shaped crystal used for data collection were  $2.3 \times 3.5 \times 0.7$  mm. For subsequent application of neutron absorption and extinction corrections, the crystal was described by eight boundary planes,  $\pm(001)$ ,  $\pm(100)$ ,  $\pm(110)$ , and  $\pm(010)$  enclosing a volume of  $1.89 \text{ mm}^3$ .

The neutron intensity data were collected on a four-circle diffractometer at the Brookhaven High Flux Beam Reactor, operating at 60 MeV, using a neutron beam obtained by the 002 reflection from a Be monochromating crystal. The neutron wavelength of  $1.05594 (15) \text{ \AA}$  was determined by a least-squares fit of  $\sin^2\theta$  data for a standard KBr crystal [ $a = 6.6000 (1) \text{ \AA}$ ]. The crystal was glued to a hollow aluminium pin fastened within a sealed aluminium can filled with He gas. The enclosure was cooled by a closed-circle refrigerator\* mounted within the diffractometer  $\chi$  circle. The lattice parameters, Table 1, were determined by a least-squares fit of  $\sin^2\theta$  data for 32 neutron reflections with  $41 < 2\theta < 56^\circ$ . The crystal temperature was set at 123 K and kept within  $\pm 0.2$  K by a temperature controller,† monitoring the temperature during the period of intensity-data collection. All reflections were measured twice ( $R_{\text{int}} = 0.012$ ). A total of 2196 reflections were measured for  $2\theta < 114^\circ$ . The scan range was  $3.0^\circ$  for  $2\theta < 58^\circ$  and  $2.6^\circ + 0.833^\circ \text{ tg } \theta$  for  $58 < 2\theta < 114^\circ$ , max.  $\sin\theta/\lambda = 0.78 \text{ \AA}^{-1}$ . Squared structure amplitudes and variances  $\sigma^2(F_o^2)$  were evaluated from  $F_o^2 = (C - B) \times \sin 2\theta$ , i.e. (counts - background),  $\sigma^2 F_o^2 = [\sigma_c^2(F_o^2) + 0.002F_o^2]$ ,  $\sigma_c(F_o^2)$  being based on counting statistics. Three standard reflections,  $< 1\%$  intensity variation.

An analytically calculated absorption correction was applied, the range of transmission factors being 0.91 to 0.98. The refinement of the atomic parameters was initiated with positions from Pedersen's (1989) low-temperature X-ray study, and assumed isotropic thermal parameters. The neutron scattering lengths, 5.805 for O, 3.67 for K, 6.648 for C, and  $-3.741$  fm for H were taken from Koester (1977). The parameters were refined by least-squares methods. The observations were given weights  $w = \sigma^{-2}(F_o^2)$  where  $\sigma^2(F_o^2)$  are the variances evaluated above. The function minimized was  $\sum w(F_o^2 - F_c^2)^2$ . The indices of fit at convergence, ( $\Delta/\sigma \leq 0.02$ ), were  $R = 0.0251$ ,  $wR = 0.0417$  and  $S = 1.332$ , with all reflections included.

A total of 61 parameters were refined, including a scale factor, positional and anisotropic thermal parameters for all six atoms. Type I anisotropic extinction correction with a Lorentzian distribution (Becker & Coppens, 1974) and anisotropy of mosaic

Table 1. *Crystal data*

Potassium oxalate monoperhydrate, $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$ , space group $C2/c$ .				
	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ (°)
Neutron, 123 K (this work)	8.858 (2)	6.505 (2)	10.872 (2)	108.38 (1)
Room temperature (Pedersen, 1967)	8.969	6.532	10.955	108.40
X-ray, 123 K (Pedersen, 1988)	8.867 (1)	6.511 (1)	10.882 (1)	108.38 (1)

Table 2. *Final positional and equivalent isotropic thermal parameters in  $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$  at 123 K*

$$U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3.$$

	$x$	$y$	$z$	$U_{\text{eq}}(\text{Å}^2)$
K	0.36031 (4)	0.34225 (5)	0.36376 (3)	0.0030
O1	0.11238 (2)	0.25033 (3)	0.08563 (2)	0.0036
O2	0.30350 (2)	0.47766 (3)	0.09066 (2)	0.0036
O3	0.45276 (2)	0.00255 (4)	0.18163 (2)	0.0037
C	0.22641 (2)	0.31753 (3)	0.05079 (1)	0.0024
H	0.51568 (5)	0.90271 (7)	0.14561 (4)	0.0068

spread described according to Thornley & Nelmes (1974) were also included. Values of the mosaic spread tensor  $Z \times 10^6$  are as follows:  $Z_{11} = 0.2063$ ,  $Z_{22} = 0.1328$ ,  $Z_{33} = 0.0495$ ,  $Z_{12} = 0.1028$ ,  $Z_{13} = -0.0345$ ,  $Z_{23} = -0.0000$ .

The final atomic parameters are given in Table 2.\* All calculations were carried out on a VAX computer using programs written or modified for the system by Lundgren (1982).

**Discussion.** The hydrogen peroxide molecule and nearest neighbours are shown in Fig. 1 which also gives the atomic notations. Bond lengths and angles are given in Table 3. The figure clearly shows the skew conformation of the hydrogen peroxide molecule in this compound in contrast to the planar conformation found in sodium oxalate monoperhydrate (Pedersen & Kvik, 1989).

The O—O distance determined,  $1.4578 (4) \text{ \AA}$ , compares very well with the dimensions found in the skew molecule in urea. $\text{H}_2\text{O}_2$  (Fritchie & McMullan, 1981) and in  $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$  (Olovsson & Templeton, 1960), solid  $\text{H}_2\text{O}_2$  (Savariault & Lehmann, 1980) and solid  $\text{D}_2\text{O}_2$  (Prince, Trevino, Choi & Farr, 1975). However, it is significantly different from the value reported by Adams *et al.* (1980),  $1.355 (8) \text{ \AA}$  as opposed to  $1.4578 (4) \text{ \AA}$  determined by us. In fact all our values are significantly different from theirs, the difference amounting to  $0.1 \text{ \AA}$  in  $\text{H}_2\text{O}_2$  and  $0.01 \text{ \AA}$  in the oxalate ion and several degrees difference in the angles, as shown in Table 3.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52154 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

\* Air Products and Chemicals Inc. Displex, model CS-202.

† Lake Shore Cryotronics Inc. model DRC 80 C, and a sensor selector, model SW 10 A.

Table 3. Geometrical data

Oxalate ion							
C—1	C—2	C—C	$\angle$ C—C—O1	$\angle$ C—C—O2	$\angle$ O1—C—O2	Reference	
1.2635 (3) Å	1.2460 (3) Å	1.5675 (5) Å	115.68 (2) <sup>a</sup>	118.36 (2) <sup>a</sup>	125.96 (2) <sup>a</sup>	a	
1.278 (12)	1.233 (9)	1.565 (9)	111.8 (5)	120.2 (7)	128.1 (7)	b	
Hydrogen peroxide molecule							
O—O	O—H	$\angle$ O—O—H	H...O	$\angle$ O—H...O	$\phi$	T	Reference
1.4578 (4) Å	1.0117 (5) Å	100.69 (3) <sup>a</sup>	1.5979 (5) Å	178.37 (4) <sup>a</sup>	101.6°	123 K	a
1.355 (8)	0.95 (1)	107.9 (8)	1.67 (1)	172.5 (9)	102 (1)	300	b

References: (a) This work; (b) Adams *et al.* (1980) (investigation of the deuterated compound).

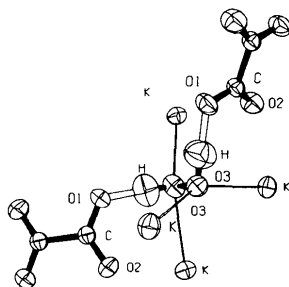


Fig. 1. Stereoscopic view of the hydrogen peroxide molecule with hydrogen bonding. Probability level of thermal ellipsoids is 99%.

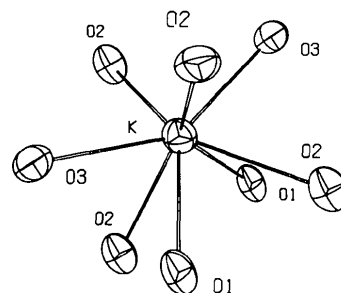
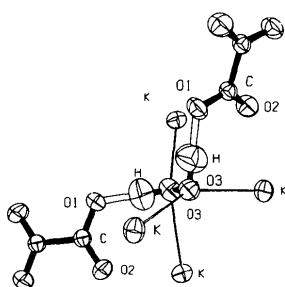


Fig. 2. The potassium ion coordination. Probability level of thermal ellipsoids is 99%.

As discussed by Pedersen (1972) the possibility of substitution of some of the  $\text{H}_2\text{O}_2$  molecules by water molecules can interfere greatly with the dimensions determined. As the two structures are isotopic it is difficult to separate the diffraction peaks due to water substitution in the powder data.

The oxalate ion is centrosymmetric and planar. The dimensions of the ion are given in Table 3.

We observe a slight difference in the C—O distances of 0.0175 (5) Å, the longest being C—O1 where O1 is the acceptor of a relatively strong hydrogen bond. An unperturbed bond should have C—O distances of equal length. The C—C distance is long, 1.5675 (5) Å, and definitely longer than in oxalic acid, 1.544 (1) Å, the value determined from low-temperature X-ray and neutron diffraction work (Stevens & Coppens, 1980). The angles around the C atoms also reflect earlier findings:  $\angle$ O—C—O larger than 120°, and  $\angle$ C—C—O1 smaller than  $\angle$ C—C—O2. These two angles correlate well with the corresponding C—O bond lengths (Pedersen, 1969).

**Potassium coordination.** The potassium ion has eight nearest neighbours in a distorted dodecahedral arrangement (Fig. 2). The K—O distances range from 2.708 (1) to 2.997 (1) Å and are of normal length.

BFP would like to thank Brookhaven National Laboratory for the neutron facilities and for

generous hospitality while staying there. The stay was made possible by a grant from the Norwegian Council for Science and Humanities, which is also hereby gratefully acknowledged. We would also like to thank Mr Joseph Henriques for valuable technical assistance.

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