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A new modification of deuterated oxalic acid dihydrate, $(COOD)_2.2D_2O$.

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Crystals of deuterated oxalic acid dihydrate, $(COOD)_2.2D_2O$, are isomorphous with those of $(COOH)_2.2H_2O$, (Robertson & Ubbelohde, 1939; Ahmed & Cruickshank 1953). Recently a nuclear magnetic resonance study was made for a single crystal of deuterated oxalic acid dihydrate by Chiba (1964). The O–D directions of this crystal, however, could not be interpreted on the basis of the ordinary structure of $(COOH)_2.2H_2O$ (hereafter called α-oxalic acid dihydrate). By X-ray study it was shown that the crystal represented a new modification of $(COOD)_2.2D_2O$. A high concentration of D_2O was essential for formation of the new modification (Chiba, 1964).

Crystals of the new form are colourless, and unstable when exposed to air. The crystal data are listed in Table 1,

Table 1. *Crystal data*

	New modification	α form
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/a$
a	$10{\cdot}04 \pm 0{\cdot}01$ Å	11·88 Å
b	$5{\cdot}06 \pm 0{\cdot}01$	3·60
c	$5{\cdot}16 \pm 0{\cdot}01$	6·12
β	$99° 12' \pm 6'$	103·5°
Z	2	2

The unit cell of the α form has been transformed in conformity with that of the new modification.

together with those of α-oxalic acid dihydrate. The intensities of X-ray reflexions were estimated visually from equi-inclination Weissenberg photographs obtained with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}542$ Å). The crystal structure was determined by the use of Harker–Kasper inequalities. The atomic coordinates are shown in Table 2. They give

Table 2. *Atomic coordinates*

	x	y	z
C	0·050	0·025	0·400
O(1)	0·039	0·199	0·249
O(2)	0·147	−0·153	0·440
O(3)	0·331	−0·077	0·151

the reliability index $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 0·13 for $h0l$ and $hk0$ reflexions.

The structure projected along the b axis is shown in Fig. 1. The oxalic acid molecules lie nearly in one plane which makes an angle of about 53° with the plane (010), whereas the corresponding angle of the α form is 29°. The oxalic acid molecules and the water molecules are linked with hydrogen bonds which make three-dimensional networks shown in Fig. 1 with broken lines. The general features of the hydrogen networks of this crystal are similar with those of α-oxalic acid dihydrate.

The hydrogen bond lengths are 2·58, 2·89 and 2·82 Å, while in α-oxalic acid dihydrate they are 2·49, 2·89 and 2·88 Å respectively. This shows that the directions of the maximum isotope effects lie near to the directions of short hydrogen bonds, as suggested by Gallagher, Ubbelohde & Woodward (1955). The hydrogen positions are roughly estimated from the difference Fourier projections on the (010) and (001) planes. They agree

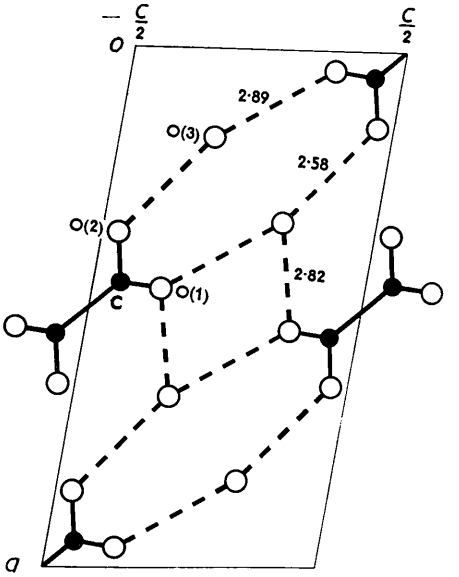

Fig. 1. Projection of the structure along the b axis.

qualitatively with the O–D directions suggested from the nuclear magnetic resonance study.

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