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The Crystal Structure of Deuterated Oxalic Acid Dihydrate $(COOD)_2.2D_2O$, by Neutron Diffraction Analysis

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The deuterium atom positions in crystals of deuterated oxalic acid dihydrate, $(COOD)_2.2D_2O$, monoclinic, with space group $P2_1/a$, $a=10{\cdot}021$, $b=5{\cdot}052$, $c=5{\cdot}148$ Å, $\beta=99{\cdot}27°$ and $Z=2$, were determined by neutron diffraction analysis. The wave-length used was 1·07 Å. Ninety reflexions from $h0l$ and $hk0$ in the range $2\theta<72°$ were measured, and the positional and isotropic thermal parameters were determined by Fourier and diagonal least-squares procedures. The bond lengths in the D_2O molecule are 0·946 and 0·960 Å with bond angle 110·5°. The O–D length of the oxalic acid molecule is 1·042 Å. The lone-pair coordination of the water molecule in $(COOD)_2.2D_2O$ (β form) is found to be different from that in $(COOH)_2.2H_2O$ (α form).

Introduction

Crystals of deuterated oxalic acid dihydrate, $(COOD)_2.2D_2O$, have been found not to be isomorphous with those of $(COOH)_2.2H_2O$ (Fukushima, Iwasaki & Saito, 1964; Fukushima, Iwasaki, Saito, Sato & Hoshino, 1965; Iwasaki & Saito, 1967). This isotope effect is expected to be closely related to the nature of hydrogen bonds. In order to compare the crystal structure of $(COOD)_2.2D_2O$ with that of $(COOH)_2.2H_2O$ including hydrogen positions, neutron diffraction analysis of $(COOD)_2.2D_2O$ has been undertaken. The hydrogen positions in $(COOH)_2.2H_2O$ had already been determined by neutron diffraction analysis (Garrett, 1954).

Experimental

A saturated solution at 29 °C was cooled slowly (1 °C per day) with seeds. After two or three days crystals of various sizes were obtained. Each sample was approximately 7 mm × 5 mm × 5 mm in dimensions. It was coated with Gryptal and enclosed in a glass tube with a drop of mother liquor. The crystal data obtained with X-rays are listed in Table 1 (Iwasaki & Saito, 1967).

Table 1. *Crystal data*

Crystal system	Monoclinic
Space group	$P2_1/a$
a	10·021 ± 0·008 Å
b	5·052 ± 0·008
c	5·148 ± 0·006
β	99·27° ± 0·07°
Z	2
V	257 Å^3

The integrated intensities were measured at the JRR-2 reactor, Japan Atomic Energy Research Institute, Tokai, using the apparatus described by Miyake, Hoshino, Suzuki, Katsuragi, Hagiwara, Yoshie & Miyashita (1962). A neutron wavelength of 1·07 Å obtained from a lead (311) monochromator was used. The spectrometer was of the θ–2θ setting and operated by step scanning at intervals of 0·1° in 2θ. The diffracted beam was detected by a BF_3 proportional counter, in conjunction with another counter for monitoring the direct beam intensity. The duration of the count at each angle was determined by the time over which the monitoring counter enumerated a given value of total count; this total count was usually 10000, but this number was increased to 20000∼40000 for the measurements of very weak intensities. Peak counting rates were about 5000 c.p.m. The integrated intensity was obtained by measuring the area of each diffraction peak over the general background.

The measurements were carried out with care so as not to overlook any weak additional spectra. The reciprocal lattice rows [100], [001], [101], [102] and [10$\bar{1}$] in the $h0l$ reciprocal lattice plane and the rows [100], [010], [110] and [210] in the $hk0$ reciprocal lattice plane were covered. Reflexions forbidden by the space group $P2_1/a$ were not observed. It was thus confirmed that the unit cell and the space group found by X-rays are true even if the deuterium atoms are considered. In the angular range $2\theta<72°$, forty-seven $hk0$ reflexions and forty-eight $h0l$ reflexions were searched for in each zone, of which ninety reflexions gave measurable intensities. All the reflexions were measured at least twice.

The usual Lorentz correction was applied to the observed intensity, but the absorption correction was not applied because the effect was negligible. At a stage of the refinements it was revealed that extinction corrections were necessary for the strong 202, 20$\bar{2}$ and 60$\bar{1}$ reflexions. In correcting them the relation

$$I_0=I\exp(-gI)$$

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was assumed, where I_0 is the observed intensity and I is the corrected intensity. The constant g was estimated graphically.

Structure determination

On the basis of a consideration of the hydrogen bonding schemes as well as of the results of the difference Fourier map of the structure of $(COOD)_2.2D_2O$ given by X-ray analysis, it was possible to propose a model for the most probable deuterium positions. Such a model was tested by a calculation of the neutron structure factors by adopting the following values for the scattering lengths: $b_C = 6{\cdot}61 \times 10^{-13}$, $b_O = 5{\cdot}77 \times 10^{-13}$, $b_D = 6{\cdot}5 \times 10^{-13}$ cm (Bacon, 1962). At the initial stage the R indices were 0·25 for $h0l$ and 0·19 for $hk0$.

The $(F_o - F_{CO})$ synthesis was carried out, where F_{CO} was the calculated structure factor taking account of all the atoms except deuterium. Figs. 1 and 2 show the

Table 2. *Atomic parameters obtained from neutron diffraction study*

	x	y	z	B	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$
C	0·0501	0·0238	0·4052	1·47	0·0005	0·0016	0·0012	0·11
O(1)	0·0371	0·1995	0·2498	2·70	0·0008	0·0021	0·0016	0·16
O(2)	0·1495	−0·1510	0·4374	2·91	0·0008	0·0031	0·0018	0·15
O(3)	0·3255	−0·0710	0·1518	3·38	0·0008	0·0029	0·0019	0·18
D(1)	0·2167	−0·1208	0·3097	2·68	0·0006	0·0023	0·0014	0·15
D(2)	0·1521	0·3278	−0·0025	2·97	0·0006	0·0023	0·0017	0·15
D(3)	0·1058	0·5563	0·7976	3·00	0·0007	0·0025	0·0016	0·15

Table 3. *Observed and calculated structure factors*

$h0l$ data

h	l	$10\|F_o\|$	$10F_c$	h	l	$10\|F_o\|$	$10F_c$
2	0	42	−44	6	4	79	52
4	0	302	−262	0	5	301	357
6	0	249	237	−2	1	210	−187
8	0	163	−163	−4	1	102	−97
10	0	304	−316	−6	1	735*	724
0	1	64	−57	−8	1	241	266
2	1	177	−147	−10	1	413	373
4	1	361	−376	−2	2	731*	−707
6	1	359	−352	−4	2	179	−205
8	1	64	−57	−6	2	73	83
0	2	167	−169	−8	2	80	−79
2	2	475*	527	−10	2	326	−335
4	2	291	−351	−2	3	97	128
6	2	336	467	−4	3	325	365
8	2	88	101	−6	3	278	−203
0	3	58	47	−8	3	64	51
2	3	294	−351	−2	4	87	78
4	3	52	56	−4	4	245	−273
6	3	118	149	−6	4	102	82
8	3	78	−73	−8	4	185	−183
0	4	116	130	−2	5	378	466
2	4	0	−28	−4	5	222	−272
4	4	75	82	−6	5	134	118

$hk0$ data

h	k	$10\|F_o\|$	$10F_c$	h	k	$10\|F_o\|$	$10F_c$
2	0	42	−44	8	2	173	−149
4	0	302	−262	9	2	42	37
6	0	249	237	10	2	83	66
8	0	163	−163	1	3	70	−53
10	0	304	−316	2	3	161	152
1	1	99	80	3	3	137	131
2	1	101	−76	4	3	52	53
3	1	351	362	5	3	90	−77
4	1	189	−158	6	3	0	−54
5	1	258	231	7	3	0	12
6	1	167	−132	8	3	174	−187
7	1	263	−264	9	3	224	−232
8	1	350	−370	0	4	136	−135
9	1	140	−129	1	4	157	−163
10	1	104	72	2	4	391	406
11	1	346	−364	3	4	244	−241
0	2	216	192	4	4	117	86
1	2	486	538	5	4	190	160
2	2	73	64	6	4	226	−145
3	2	319	−355	7	4	190	161
4	2	0	−50	1	5	227	224
5	2	451	−454	2	5	79	−67
6	2	232	−216	3	5	188	226
7	2	144	143	4	5	65	65

* Correction was applied for extinction effect.

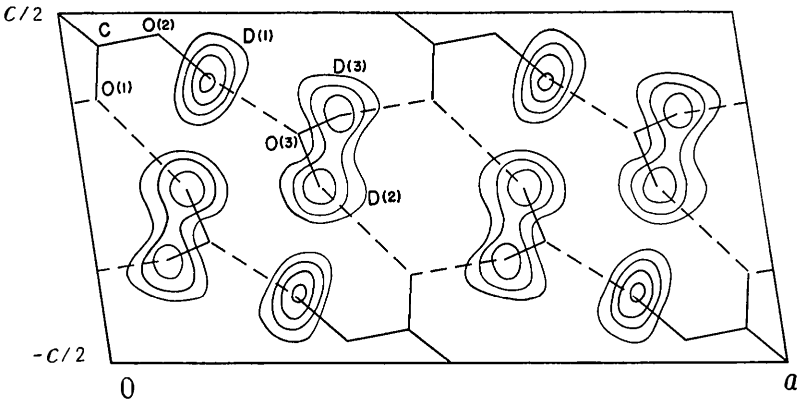


Fig. 1. $(F_o - F_{CO})$ synthesis, projected along the b axis, showing the neutron scattering density due to the deuterium atoms only. The contours are at intervals of 5×10^{-13} cm.Å^{-2}, starting with the zero contour.

$(F_o - F_{CO})$ syntheses projected along the *b* and *c* axes respectively. By taking account of the deuterium positions suggested by these projections, *R* indices were reduced to 0·20 and 0·15 respectively. The positional parameters and individual isotropic temperature factors were refined by a series of two-dimensional Fourier syntheses and difference syntheses. Finally a diagonal least-squares refinement was carried out with isotropic temperature factors. The atomic parameters thus obtained are listed in Table 2. The final *R* indices were 0·108 for *h*0*l* and 0·105 for *hk*0 reflexions. Final neutron scattering density projections are shown in Figs. 3 and 4. The observed and calculated structure factors are given in Table 3. Data of the isotropic temperature factors for deuterium atoms obtained from the above analysis have been compiled in Table 3 of the paper of Iwasaki & Saito (1967).

Description of the structure

In Table 4 are listed the positional parameters, in which the coordinates of carbon and oxygen are taken from the X-ray results (Iwasaki & Saito, 1967), and the deuterium positions from the results of the present neutron diffraction study. *R* indices based on these parameters are 0·125 for *h*0*l* and 0·129 for *hk*0. These atomic parameters were employed in the calculation of the molecular dimensions. The interatomic distances and the bond angles related to the deuterium atoms are given in Table 5.

Oxalic acid molecule

It was shown that the structure consists of discrete water and acid molecules with no evidence of disordering of hydrogen positions or of the presence of OD_3^+

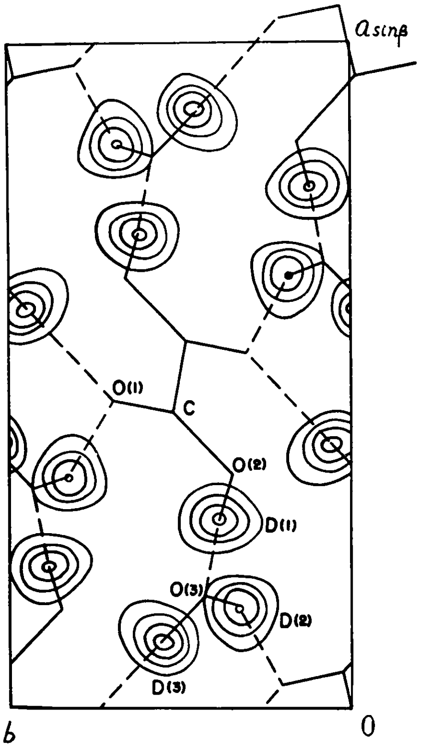


Fig. 2. $(F_o - F_{CO})$ synthesis projected along the *c* axis.

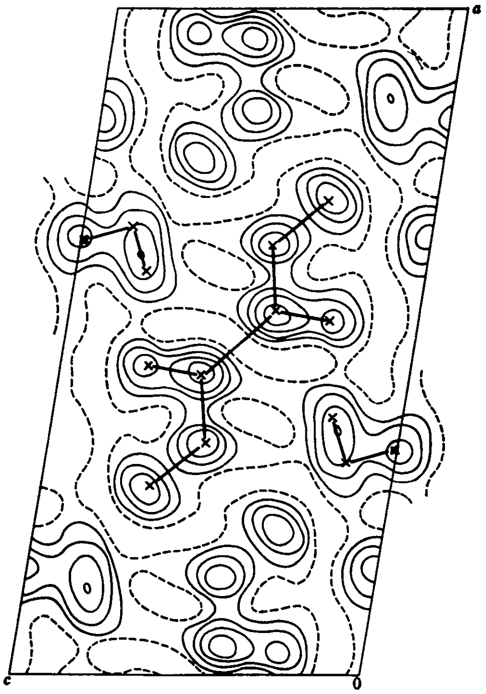


Fig. 3. Neutron scattering density projection along the *b* axis. The contours are at intervals of 4×10^{-13} cm.Å^{-2}, and broken lines are zero contours.

Table 4. *Final atomic coordinates*

The positions of the carbon and oxygen atoms are obtained from X-ray study and those of the deuterium atoms are obtained from neutron diffraction study.

	x	*y*	*z*	σ(*x*)	σ(*y*)	σ(*z*)
C	0·0503	0·0230	0·4040	0·0003	0·0007	0·0006
O(1)	0·0371	0·2002	0·2464	0·0002	0·0005	0·0005
O(2)	0·1466	−0·1519	0·4360	0·0002	0·0005	0·0005
O(3)	0·3281	−0·0793	0·1511	0·0003	0·0006	0·0005
D(1)	0·2167	−0·1208	0·3097	0·0006	0·0023	0·0014
D(2)	0·1521	0·3278	−0·0025	0·0006	0·0023	0·0017
D(3)	0·1058	0·5563	0·7976	0·0007	0·0025	0·0016

ions, although these molecules are linked to each other by intermolecular hydrogen bonds.

Including deuterium, the oxalic acid molecule has a center of symmetry and is completely planar. The deviation of the deuterium atom from the molecular plane through the carbon and oxygen atoms is 0·02 Å. The equation of the best plane obtained by least squares for carbon, oxygen and deuterium atoms is,

$$2{\cdot}891X+1{\cdot}989Y+2{\cdot}000Z=1\,,$$

where X, Y and Z are the fractional coordinates referred to the crystal axes a, b and c. The deviation of each atom from this plane is listed in Table 6.

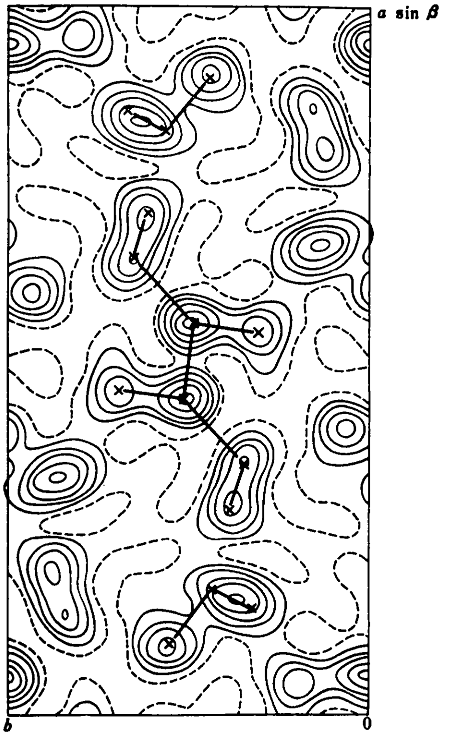
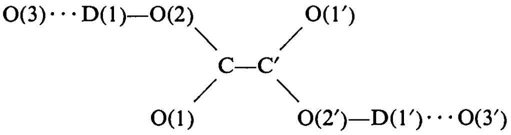


Fig. 4. Neutron scattering density projection along the c axis.

Table 6. *Deviations of the atoms from the best plane through the oxalic acid molecule* $(COOD)_2$

$2{\cdot}891X+1{\cdot}989Y+2{\cdot}000Z=1$

Atom	Deviation	Atom	Deviation
C	−0·0014 Å	C′	0·0014 Å
O(1)	−0·0027	O(1′)	0·0026
O(2)	−0·0095	O(2′)	0·0094
D(1)	0·007	D(1′)	−0·007
O(3)	0·1415	O(3′)	−0·1415



The hydroxyl O–D bond is found to be 1·042 Å in length. It is slightly shorter than that in $(COOH)_2.2H_2O$ (1·057 Å) (Garrett, 1954).

Water molecule

The O–D bond lengths in the D_2O molecule (0·946 and 0·960 Å) are not significantly different from, but are slightly shorter than, that in deuterated ice determined by neutrons (1·01 Å) (Peterson & Levy, 1953, 1957). These O–D bond lengths are very close to those

Table 5. *Interatomic distances and bond angles related to the deuterium atoms*

		$(COOH)_2.2H_2O$	
	$(COOD)_2.2D_2O$ Present work	X-rays (Ahmed *et al.*)	Neutrons (Garrett)
O(2)–D(1)	1·042 ± 0·008 Å		1·057 Å
O(3)–D(2)	0·946 ± 0·010		0·968
O(3)–D(3)	0·960 ± 0·010		0·945
D(1)· · ·D(3)	2·136 ± 0·011		
D(1)· · ·D(2)	2·795 ± 0·015		
D(2)· · ·D(3)	1·566 ± 0·015		
D(1)· · ·O(3)	1·500 ± 0·008		1·463
D(2)· · ·O(1)	1·965 ± 0·009		1·944
D(3)· · ·O(1)	1·874 ± 0·010		1·911
D(3)· · ·O(2)	2·460 ± 0·011		
O(2)–[D(1)]· · ·O(3)	2·540 ± 0·004	2·491	2·518
O(1)· · ·[D(2)]–O(3)	2·854 ± 0·005	2·885	2·856
O(1)· · ·[D(3)]–O(3)	2·822 ± 0·004	2·879	2·840
∠ D(2)O(3)D(3)	110·54 ± 0·87°		105°41′
∠ CO(2)D(1)	112·29 ± 0·47		112 56
∠ D(1)O(3)D(2)	130·01 ± 0·68		118 04
∠ D(1)O(3)D(3)	119·42 ± 0·69		113 07
∠ O(2)D(1)O(3)	174·37 ± 0·64		175 21
∠ O(3)D(2)O(1)	155·83 ± 0·68		156 06
∠ O(3)D(3)O(1)	169·10 ± 0·84		167 02

found in the H_2O molecule in $(COOH)_2.2H_2O$ (0·945 and 0·968 Å) and to those in water vapor (0·96 Å) (Wells, 1962). The observed bond angle DOD (110·5°), however, differs from the value derived from the structure of $(COOH)_2.2H_2O$ (105·7°), but is similar to that in deuterated ice (109·5°).

Hydrogen bonding

The oxygen atom of the D_2O molecule behaves as an acceptor for a short hydrogen bond O(2)–D(1)···O(3) (2·540 Å), in which the D(1) atom lies very close to the line joining O(2) and O(3). The angle O(2)D(1)-O(3) is 174·4° as is expected for such a strong hydrogen bond. The O(2)–D(1) bond length is 1·042 Å, in conformity with the value expected from the empirical O···O distance *versus* O–H distance curve of Atoji & Rundle (1958) and Bacon (1963) (Fig. 5). This hydrogen bond in the crystal of $(COOD)_2.2D_2O$ appears to be slightly weaker than the corresponding hydrogen bond of $(COOH)_2.2H_2O$. This is consistent with the fact that the O–D distance (1·042 Å) is slightly shorter than the O–H length (1·057 Å) in $(COOH)_2.2H_2O$.

The O–D distances in the water molecule (0·946 and 0·960 Å) are found to be close to the 0·96 Å value for gaseous H_2O and the O(1)···D(2)–O(3) and O(1)···D(3)–O(3) bonds are far from linear (155·8 and 169·1°). Therefore, the attractive forces involved in these bonds would be considerably weaker than that between water oxygen and hydroxyl group in the oxalic acid molecule. Comparison of the O(3)D(3)O(1″) angle of 169° with the value 156° found in O(3)D(2)O(1′) seems to indicate that the former hydrogen bond is somewhat stronger. This is also consistent with the distances of approach between D(3)···O(1″) and D(2)···O(1′), 1·874 and 1·965 Å respectively.

The distances of the O(3)–D(3)···O(2″) and the D(3)···O(2″) bonds are very close to the normal O···O and O···H van der Waals contacts. This fact suggests that the deuterium atom D(3) interacts only with the O(1) atom of a neighboring oxalic acid molecule, and does not form a bifurcated hydrogen bond.

Discussion

The crystal structure of β-$(COOD)_2.2D_2O$ is shown in Fig. 6, together with that of α-$(COOH)_2.2H_2O$. The interatomic distances and bond angles of the latter form are taken from Ahmed & Cruickshank (1953) and Garrett (1954).

The results of nuclear magnetic resonance study (Chiba, 1964) are well explained by the structure of the β form. The direction cosines of the O–D bonds in Table 7 obtained in the present investigation agree well with the direction cosines of the maximum field gradient determined by the nuclear magnetic resonance study.

The hydrogen bond O(2)–D(1)···O(3) is not of the symmetric type. The hydrogen (deuterium) atom is definitely associated with the carboxyl group in both α and β forms. It has been reported that the hydrogen bond in the crystals of $DCrO_2$ is asymmetric. Although there is so far no successful neutron diffraction study concerning the hydrogen positions in $HCrO_2$, an infrared spectroscopic study has suggested that the hydrogen bond in this structure would probably be symmetric (Snyder & Ibers, 1962; Hamilton & Ibers, 1963). The structure of deuterated resorcinol is just the same as that of the unstable β form of $C_6H_4(OH)_2$ (Robertson, 1938). Thus, the different crystal structures of $(COOD)_2.2D_2O$ and α-$(COOH)_2.2H_2O$ present a novel example of the isotope effect. These two forms seem to have no direct relationship in structure with each other. The measurement of the thermal expansion of the α-$(COOH)_2.2H_2O$ gave no evidence of the phase transition between 90 and 293°K, such as $\alpha \rightleftharpoons \beta$ (Robertson & Ubbelohde, 1939).

The elongation of the shorter hydrogen bond by the substitution of H by D can also be observed in the case of β-$(COOD)_2.2D_2O$. Two values for the bond distance of O(2)–H(1)···O(3) in α-$(COOH)_2.2H_2O$ have been reported: 2·491 (Ahmed & Cruickshank, 1953) and 2·518 Å (Garrett, 1954). The O(2)–D(1)···O(3) length found in the β form is 2·540 Å, which exceeds either of the two values given above by an amount which is significantly greater than the e.s.d. On the other hand the longer hydrogen bonds O(1)···D(2)–O(3) (2·854 Å) and O(1)···D(3)–O(3) (2·822 Å) do not indicate such an elongation due to the isotope

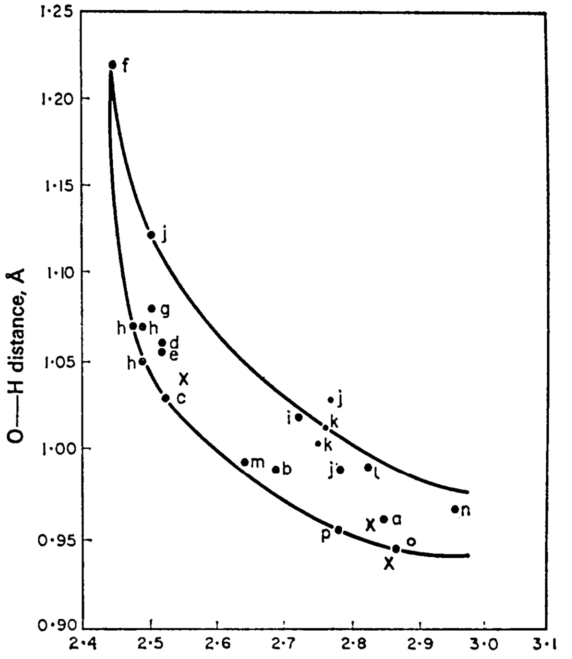


Fig. 5. The correlation diagram between O–H and O–H···O distances. (*a*, *e*) $(COOH)_2.2H_2O$ (*b*) α-HIO_3 (*c*) KD_2PO_4 (*d*) KH_2AsO_4 (*f*) nickel dimethyl-glyoxime (*g*, *h*) KH_2PO_4 (*i*) α-resorcinol (*j*) $Na_2CO_3.NaHCO_3.2H_2O$ (*k*) ice (*l*) $CaSO_4.2H_2O$ (*m*) AlO(OH) (*n*, *o*) $Li_2SO_4.H_2O$ (*p*) $CuSO_4.5H_2O$ (average). × corresponds to $(COOD)_2.2D_2O$.

effect. These bond lengths are even shorter than those corresponding to the α form. Consequently the isotope effect can be seen most remarkably in the shorter hydrogen bonds. It is interesting to see that this effect still exists even in the case where the alteration of the crystal structure occurs.

Another important difference between the structures of the α and the β forms is that concerning the environment of the water molecule. The sum of the bond angles D(2)O(3)D(3), D(1)O(3)D(2) and D(1)O(3)D(3) of the β form is 360°. Thus, three deuterium atoms and the water oxygen atom lie in one plane. The corresponding sum of the three angles in the α form is 340°. In the latter form, the direction of the line joining the water oxygen atom and the carboxyl hydrogen atom [O(3)· · · H(1)] makes an angle of 50·5° with the plane of the water molecule. These relationships are illustrated in Fig. 7.

The oxygen atom in the water molecule has two O–H orbitals and two lone-pair orbitals directed toward the opposite side to the O–H bonds. They can be described by nearly tetrahedral orbitals. In hydrates, the O–H orbitals are generally used to form the hydrogen bonds. In the case of α-$(COOH)_2.2H_2O$, one of the lone pairs is specifically directed toward the donor group of a hydrogen bond, while the other is not. For β-$(COOD)_2.2D_2O$ the bisector of the lone pairs is directed toward the donor group of a hydrogen bond. The difference of these lone-pair coordinations corresponds to the observed difference in the bond angles of DOD (110·5°) and HOH (105·7°) of α-$(COOH)_2.2H_2O$. Slightly higher values of the HOH angle are

Table 7. *Direction cosines of the* O–D *bonds*

Direction cosines of the maximum field gradient are listed in the case of the n.m.r. study. Signs of these values are given in conformity with those obtained from the present study.

		Present study			Nuclear magnetic resonance study (Chiba)		
		$\cos\theta_b$	$\cos\theta_c$	$\cos\theta_{a^*}$	$\cos\theta_b$	$\cos\theta_c$	$\cos\theta_{a^*}$
O(2)–D(1)	acid	0·150	−0·729	0·662	0·156	−0·739	0·655
O(3)–D(2)	water	−0·493	−0·845	0·208	−0·512	−0·844	0·159
O(3)–D(3)	water	0·714	0·165	0·683	0·710	0·139	0·691

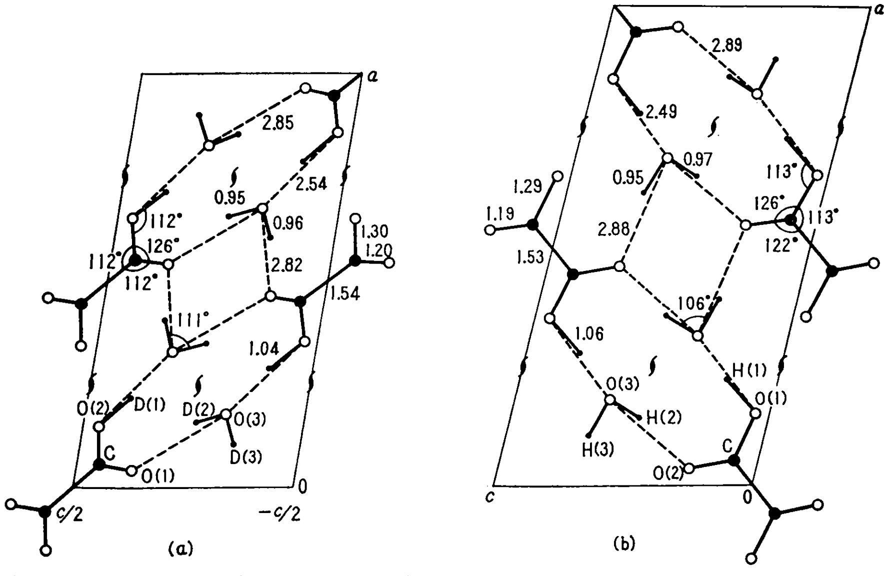


Fig. 6. The structure projected along the *b* axis. (*a*) $(COOD)_2.2D_2O$, (*b*) $(COOH)_2.2H_2O$.

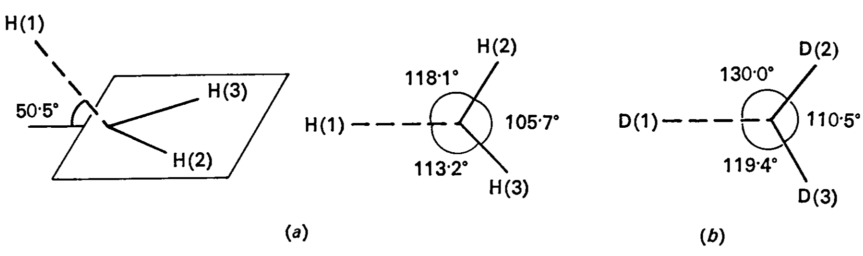


Fig. 7. The environment of the oxygen atom of the water molecule in α and β forms. (*a*) $(COOH)_2.2H_2O$ (α form), (*b*) $(COOD)_2.2D_2O$ (β form).

reported also in other substances in which the bisector of the lone-pairs is directed toward a metal ion or toward a hydrogen bond donor group (Chidambaram, Sequeira & Sikka, 1964).

The replacement of hydrogen by deuterium should have very little effect on the lattice energy if the crystal structure is the same. The major effect of the replacement then will be the difference in the zero point energy. In a flat and highly asymmetric potential field in which the hydrogen atom moves, the higher zero point energy of the proton will be associated with an increase of the OH length over the OD. The difference in the zero point energy affects the strength of the hydrogen bond, as indicated theoretically by Gallagher (1959) and Reid (1959). In the case of oxalic acid dihydrate, however, the difference of the vibration energy is so large that the effect is not sufficiently compensated by the elongation of the short hydrogen bond alone but necessitates a transformation into a more stable crystal structure. In α-$(COOH)_2.2H_2O$, the hydrogen bond between the hydroxyl group of the oxalic acid molecule and the oxygen atom of the water molecule is strong enough for one of the lone-pairs to be specifically directed toward the donor group. In β-$(COOD)_2.2D_2O$, on the other hand, the corresponding hydrogen bond is slightly weaker so that it seems to be rather unfavorable for only one of the lone-pairs to be specifically directed. Consequently the bisector of two lone-pairs is directed toward a hydrogen donor group These small changes in the interatomic force seems to alter the entire crystal structure.

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The Crystal Structure of $Pu_2\,Zn_{\sim 9}$*

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$Pu_2Zn_{\sim 9}$ has a hexagonal subcell with $a=14{\cdot}43$ and $c=14{\cdot}14$ Å, probable space group $P6_3/mmc$. The true unit cell appears to be hexagonal with a doubled a axis but this apparent hexagonal symmetry may result from twinning. A reasonable solution has been obtained for the subcell and leads to the formula $Pu_{13}Zn_{58}$ or $PuZn_{4{\cdot}46}$. The subcell is similar to and probably isostructural with recently reported phases $Ce_2Cd_{\sim 9}$, $Ce_2Zn_{\sim 9}$ and $Y_2Zn_{\sim 9}$.

Introduction

As part of an investigation of binary phase diagrams being carried out in this Laboratory, the Pu–Zn system has been studied. Four zinc-rich phases, $PuZn_2$, $Pu_2Zn_{\sim 9}$, $PuZn_8$ and Pu_2Zn_{17} have been reported by Cramer, Ellinger & Land (1960). Recently, Cramer & Wood (1966) have found evidence of other phases in the high-zinc region of the phase diagram. The rather complex phase $Pu_2Zn_{\sim 9}$ is the subject of the present report.

While this work was in progress, Elliott & Lemons (1964) found, through vapor pressure measurements, a series of 'microphases' in the Ce–Cd system near

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