SHORT COMMUNICATIONS

Neutron Diffraction Study of Deuterated Oxalic Acid Dihydrate, $(COOD)_2 \cdot 2D_2O$

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(Received October 27, 1964)

Crystals of deuterated oxalic acid dihydrate, $(COOD)_2 \cdot 2D_2O$, have been found not to be isomorphous[1,2] with those of $(COOH)_2 \cdot 2H_2O$.[3] The crystal structure of the former was determined by X-ray study.[1]

This isotope effect is expected to be closely related to the nature of the hydrogen bonds. A neutron diffraction study has thus been undertaken in order to determine the deuteron positions and to investigate the difference between the hydrogen bonds in the two structures.

Anhydrous oxalic acid was dissolved in D_2O

1) F. Fukushima, H. Iwasaki and Y. Saito, *Acta Cryst.*, in press; This Bulletin, to be published.
2) T. Chiba, *J. Chem. Phys.*, **41**, 1352 (1964).
3) J. M. Robertson and A. R. Ubbelohde, *Proc. Roy. Soc.*, **A170**, 222 (1939); F. R. Ahmed and D. W. J. Cruickshank, *Acta Cryst.*, **6**, 385 (1953); R. S. Garrett, Oak Ridge National Laboratory Report, No. 1745 (1954).

with warming, and the water was evaporated in vacuo. This procedure was repeated three times, then the rhomboidal crystals of $(COOD)_2 \cdot 2D_2O$ were obtained. A high concentration of D_2O was necessary to the formation of these crystals.[2]

The crystal data obtained with X-rays (Cu$K\alpha$, $\lambda = 1.542$ Å) are listed in Table I.

TABLE I. CRYSTAL DATA

	$(COOD)_2 \cdot 2D_2O$	$(COOH)_2 \cdot 2H_2O$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/a$
a	10.04±0.01 Å	11.88 Å
b	5.06±0.01	3.60
c	5.16±0.01	6.12
β	99°12′±6′	103.5°
Z	2	2

For the neutron diffraction work, crystals approximately $5 \times 5 \times 2$ mm^3 in dimensions were grown slowly from a supersaturated solution. They are colorless and unstable when exposed to air. The specimens were coated with a glyptal film and enclosed in glass tubes with a drop of mother liquor. The integrated intensities were measured at the JRR-2 reactor, Japan Atomic Energy Research Institute, Tokai, using the apparatus described by Miyake et al.[4] A neutron wavelength of 1.057 Å was obtained by means of a lead monochromator. The 27 reflections $0kl$ and the 26 reflections $h0l$ were observed in each zone for which $2\theta < 65°$.

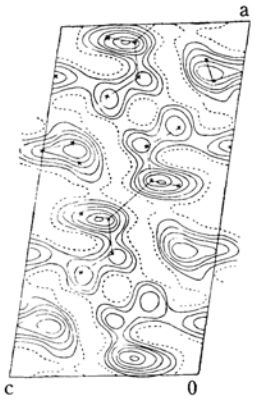

Fig. 1. Fourier projection along the b axis.

The approximate deuteron positions were found by the Fourier method, assuming the carbon and oxygen parameters derived from the X-ray analysis. Then $(F_o - F_{C,O})$ synthesis was carried out, where $F_{C,O}$ was the calculated contribution to the structure factor of all the atoms except deuteron. Figures 1 and 2 show

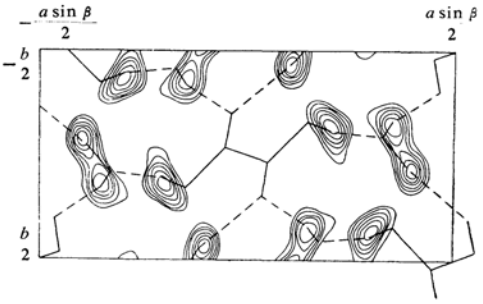

Fig. 2. $(F_o - F_{C,O})$ synthesis projected along the c axis.

the Fourier projection along the b axis and the $(F_o - F_{C,O})$ synthesis projected along the c axis respectively. The atomic co-ordinates are listed in Table II. They give the reliability index, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, of 0.19. These deuteron parameters agree with those obtained from the difference synthesis of X-ray data[1]

TABLE II. ATOMIC CO-ORDINATES

	x	y	z
C	0.052	0.023	0.404
O (1)	0.037	0.196	0.248
O (2)	0.150	−0.157	0.438
O (3)	0.328	−0.080	0.150
D (1)	0.205	−0.113	0.294
D (2)	0.146	0.330	0.002
D (3)	0.112	0.548	0.788

and with the O–D directions suggested from the nuclear magnetic resonance study.[2]

Refinements are now going on. Further experiments are in progress to collect more reflection data. Full details will be reported later.

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4) S. Miyake, S. Hoshino, K. Suzuki, H. Katsuragi, S. Hagiwara, T. Yoshie and K. Miyashita, *J. Phys. Soc. Japan*, **17**, *Suppl.* B-II, 358 (1962).