

Packing

The packing of molecules is shown in Fig. 4 in a projection along [010]. The main features of the structure are the hydrogen bonds, running in the direction [101]. This hydrogen-bond network is illustrated in Fig. 5. The chloride ion is trapped between two molecules of vindolinine and linked by two symmetrical hydrogen bonds involving the protonated nitrogen N(4). The geometry of these bonds: $N^+ \cdots Cl^- = 3.07$, $H \cdots Cl^- = 2.07$ Å and $N-H \cdots Cl = 176^\circ$ indicates a fairly strong hydrogen bond. The perchlorate ion, on the other hand, accepts two symmetrical H bonds: $N(1)-H \cdots O(27) = 3.05$ Å, $N-H \cdots O = 156^\circ$.

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Magnesium Formate Dihydrate: a Crystal Structure Redetermination at 130 and 293 K

BY G. DE WITH, S. HARKEMA AND G. J. VAN HUMMEL

Chemical Physics Laboratory, Twente University of Technology, P.O. Box 217, Enschede, The Netherlands

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The structure of magnesium formate dihydrate has been redetermined at approximately 130 and 293 K by X-ray methods. The structure as proposed by Osaki, Nakai & Watanabé [*J. Phys. Soc. Japan* (1964), **19**, 717–723] proved to be essentially correct. H atoms are located and accurate values of parameters are presented.

Introduction

Some structural research has been carried out on metal formates in our laboratory. Structures investigated so far include lithium formate monohydrate (Enders-Beumer & Harkema, 1973) and sodium formate (Enders-Beumer & Harkema, 1976). In this paper we present the redetermination of the crystal structure of magnesium formate dihydrate at approximately 130 and 293 K.

Experimental

Small, single crystals of the title compound with linear dimensions of about 0.4 mm were grown by slow evaporation of a solution obtained by neutralizing aqueous formic acid with magnesium carbonate.

Data were obtained on a Philips PW1100 computer-controlled automatic four-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. The $\omega/2\theta$ scanning technique in the θ range 3 – 27° was used throughout. A detector aperture of 2° horizontally and 1° vertically was chosen.

At 130 K, 1304 reflexions were measured at a rate of 0.1° s^{-1} and a scan angle of 2° . 1158 reflexions had an intensity greater than twice the standard deviation as estimated from counting statistics.

At 293 K, 1310 reflexions were measured at a rate of $0.08^\circ \text{ s}^{-1}$ and a scan angle of 1.5° . Here 1184 reflexions had intensities greater than twice the standard deviation. In both cases no significant systematic change in standard reflexions was observed during the measurement.

The space group $P2_1/c$ as found by earlier workers (Osaki, Nakai & Watanabé, 1964) has been confirmed (from systematic absences: $h0l$ with l odd and $0k0$ with k odd). Unit-cell information is given in Table 1.

Structure refinement

Full-matrix least-squares refinement was carried out with a modification of the program *ORFLS* (Busing,

Martin & Levy, 1962). The function minimized was $\sum \omega(|F_o| - k|F_c|)^2$, where the summation extends over all reflexions with intensities greater than twice their standard deviations, k is a scaling factor, $|F_o|$ the observed structure factor and $|F_c|$ the calculated structure factor. The weight, ω , for each reflexion was taken to be $\omega = \sigma^{-2}$, where σ is the estimated standard deviation of the structure factor. σ was estimated as $2S + 0.01|F_o|$ where S denotes the standard deviation in $|F_o|$ due to counting statistics.

Structure and isotropic thermal parameters as published earlier (Osaki, Nakai & Watanabé, 1964) served as input. After refinement with anisotropic thermal parameters, a difference Fourier map was calculated which showed the positions of all H atoms. Atomic scattering factors for C and O as calculated (Harkema, 1971) from accurate atomic wave functions (Clementi, 1965) were used. The scattering factor for Mg^{2+} was taken from *International Tables for X-ray Crystallography* (1962) and that for H from the work by Stewart, Davidson & Simpson (1965).

In the last stage of refinement an isotropic correc-

Table 1. *Unit-cell information*

Here and in the following tables the standard deviation in the last digits is given in parentheses.

	130 K	293 K
a	8.616 (5) Å	8.640 (5) Å
b	7.107 (3)	7.149 (3)
c	9.400 (7)	9.382 (7)
β	98.46 (1)°	98.05 (1)°
V	569.3 Å ³	573.8 Å ³
D_x	1.731 g cm ⁻³	1.717 g cm ⁻³
D_m	—	1.797
Z	4	4

Table 2. *Positional and thermal parameters at 130 K*

All U values are given in Å². All other values are $\times 10^4$. The anisotropic temperature factor used for the heavy atoms was: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$. The isotropic temperature factor used for hydrogen atoms was: $\exp(-8\pi^2U_{11}\sin^2\theta/\lambda^2)$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mg(1)	0	0	0	59 (4)	68 (5)	56 (5)	-4 (4)	4 (3)	-1 (4)
Mg(2)	$\frac{1}{2}$	$\frac{1}{2}$	0	56 (4)	77 (5)	77 (6)	9 (4)	9 (3)	-3 (4)
C(1)	316 (2)	2273 (3)	2714 (2)	109 (9)	90 (9)	129 (10)	7 (8)	-12 (8)	-9 (8)
C(2)	3268 (2)	6137 (3)	4363 (2)	110 (10)	113 (10)	106 (10)	4 (8)	-8 (7)	3 (8)
O(1)	943 (2)	1109 (2)	1973 (1)	98 (7)	93 (7)	87 (7)	8 (5)	6 (5)	-26 (6)
O(2)	844 (2)	2737 (2)	3985 (1)	107 (7)	98 (7)	75 (7)	8 (5)	0 (5)	-17 (6)
O(3)	4369 (1)	7258 (2)	4241 (2)	79 (6)	112 (7)	143 (8)	-31 (6)	33 (5)	-17 (6)
O(4)	2100 (2)	6494 (2)	4992 (1)	80 (7)	107 (7)	114 (7)	-16 (6)	20 (5)	5 (6)
O(5)	2794 (2)	4783 (2)	646 (2)	90 (7)	98 (8)	145 (8)	-15 (6)	10 (6)	-12 (6)
O(6)	4137 (2)	1074 (2)	3021 (2)	72 (7)	251 (9)	118 (8)	-14 (6)	-2 (6)	56 (7)
H(1)	2283 (36)	4109 (44)	225 (32)	322 (91)	—	—	—	—	—
H(2)	2340 (37)	5930 (46)	486 (32)	423 (89)	—	—	—	—	—
H(3)	3313 (27)	4889 (34)	3898 (26)	174 (62)	—	—	—	—	—
H(4)	9252 (32)	2932 (41)	2261 (32)	401 (83)	—	—	—	—	—
H(5)	4656 (41)	1512 (48)	2297 (40)	603 (108)	—	—	—	—	—
H(6)	3252 (38)	933 (40)	2721 (30)	308 (82)	—	—	—	—	—

Table 3. *Positional and thermal parameters at 293 K*

See Table 2 for temperature factors.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mg(1)	0	0	0	123 (3)	101 (3)	102 (3)	2 (2)	0 (2)	0 (3)
Mg(2)	$\frac{1}{2}$	$\frac{1}{2}$	0	121 (3)	149 (4)	162 (4)	12 (3)	7 (3)	-7 (3)
C(1)	348 (2)	2305 (2)	2693 (2)	228 (8)	200 (7)	210 (8)	44 (6)	-57 (6)	-65 (7)
C(2)	3259 (2)	6165 (2)	4385 (2)	192 (7)	179 (8)	265 (9)	-14 (6)	7 (6)	-32 (6)
O(1)	950 (1)	1127 (1)	1967 (1)	193 (5)	194 (5)	156 (5)	11 (4)	-1 (4)	-57 (4)
O(2)	848 (1)	2770 (2)	3962 (1)	214 (5)	188 (6)	150 (5)	38 (4)	-16 (4)	-47 (4)
O(3)	4356 (1)	7273 (2)	4259 (1)	183 (5)	207 (6)	335 (7)	-58 (4)	83 (5)	-53 (5)
O(4)	2091 (1)	6516 (1)	4993 (1)	153 (5)	203 (6)	236 (7)	-37 (4)	33 (4)	-2 (5)
O(5)	2796 (1)	4751 (2)	635 (1)	176 (6)	192 (6)	285 (6)	-16 (5)	26 (5)	-4 (5)
O(6)	4149 (2)	1044 (2)	3008 (1)	165 (6)	510 (9)	233 (7)	-4 (6)	1 (5)	143 (6)
H(1)	2223 (27)	3988 (32)	211 (23)	444 (66)	—	—	—	—	—
H(2)	2385 (28)	5753 (36)	500 (24)	497 (71)	—	—	—	—	—
H(3)	3326 (23)	4905 (28)	3971 (21)	378 (55)	—	—	—	—	—
H(4)	9289 (26)	2917 (34)	2297 (25)	599 (69)	—	—	—	—	—
H(5)	4616 (28)	1434 (32)	2357 (26)	505 (70)	—	—	—	—	—
H(6)	3230 (32)	964 (32)	2715 (24)	492 (68)	—	—	—	—	—

tion for secondary extinction was applied (Larson, 1969). No absorption correction was performed ($\mu = 2.81 \text{ cm}^{-1}$). The final R values are, at 130 K: $R = 3.6$, $R_w = 4.1\%$; at 293 K: $R = 2.9$, $R_w = 3.4\%$. * Final parameters are given in Tables 2 (130 K) and 3 (293 K).

Description of the structure

The structure as proposed by Osaki, Nakai & Watanabé (1964) proved to be correct. The Mg ions in the structure occupy the special positions (a) and (d) as denoted in *International Tables for X-ray Crystallography* (1952). Both types of Mg ions are surrounded octahedrally by six O atoms.

The first Mg ion (lying on a centre of symmetry) is surrounded by six O atoms of different formate ions. Bond lengths and angles related to this octahedron are given in Table 4. The coordination around this Mg ion is shown in Fig. 1.

Table 4. Bond distances (Å) and angles (°) in the oxygen octahedra

	130 K	293 K
Octahedron 1		
Mg(1)—O(4)	2.099 (1)	2.108 (1)
Mg(1)—O(2)	2.057 (1)	2.056 (1)
Mg(1)—O(1)	2.069 (1)	2.075 (1)
O(4)—Mg(1)—O(2)	91.72 (5)	91.99 (4)
O(4)—Mg(1)—O(1)	88.33 (5)	88.29 (4)
O(2)—Mg(1)—O(1)	89.95 (5)	89.84 (4)
Octahedron 2		
Mg(2)—O(3)	2.118 (1)	2.118 (1)
Mg(2)—O(5)	2.084 (1)	2.081 (1)
Mg(2)—O(6)	2.047 (2)	2.051 (1)
O(3)—Mg(2)—O(5)	80.23 (6)	78.83 (5)
O(3)—Mg(2)—O(6)	89.78 (6)	89.53 (5)
O(5)—Mg(2)—O(6)	93.86 (6)	93.82 (5)

The second Mg ion, also on a centre of symmetry, is surrounded by four O atoms from water molecules and two O atoms of formate groups, as depicted in Fig. 2. Data pertaining to this unit are also given in Table 4.

The oxygen octahedra are quite regular as far as bond lengths and angles are concerned. The bond lengths found are in the range commonly found for octahedrally surrounded Mg (Flack, 1973). The different octahedra are linked together by formate ions, each of which takes part in the coordination of two Mg ions. There also exist hydrogen bonds between different coordination octahedra.

The first formate ion [consisting of O(1), O(2), C(1) and H(4)] is coordinated to two different Mg(1) ions. Bond lengths and angles in this ion are given in Table

5. The O atoms act as acceptors of hydrogen bonds from two water molecules. Coordination and hydrogen bonding to this ion are given in Fig. 3.

The second formate ion [O(3), O(4), C(2) and H(3)] is part of the coordination sphere around two different Mg ions [Mg(1) and Mg(2)]. This formate ion is also accepting two hydrogen bonds from water molecules as Fig. 4 shows. The data given in Table 5 show hardly any difference in the geometry of the two

Table 5. Bond distances (Å) and angles (°) in the formate ions

	130 K	293 K
Formate 1		
C(1)—O(1)	1.254 (2)	1.241 (2)
C(1)—O(2)	1.258 (3)	1.254 (3)
C(1)—H(4)	1.06 (3)	1.04 (2)
O(1)—C(1)—O(2)	125.1 (2)	125.9 (2)
O(1)—C(1)—H(4)	119.1 (1.7)	120.5 (1.5)
O(2)—C(1)—H(4)	115.8 (2.3)	113.4 (1.8)
Formate 2		
C(2)—O(3)	1.257 (2)	1.254 (2)
C(2)—O(4)	1.265 (2)	1.252 (2)
C(2)—H(3)	0.99 (2)	0.99 (2)
O(3)—C(2)—O(4)	125.3 (2)	125.8 (2)
O(3)—C(2)—H(3)	116.5 (1.6)	117.0 (1.3)
O(4)—C(2)—H(3)	118.1 (1.7)	117.3 (1.4)

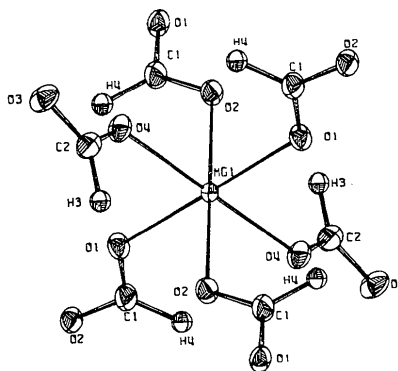


Fig. 1. The coordination of Mg(1).

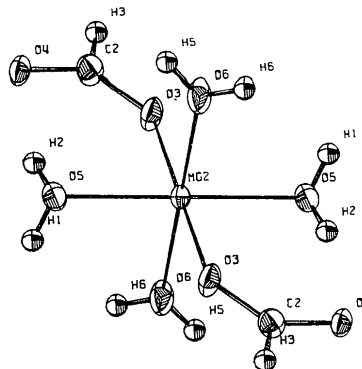


Fig. 2. The coordination of Mg(2).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31659 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

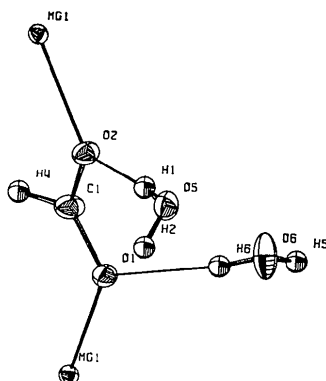


Fig. 3. Hydrogen bonding and coordination of formate ion (1).

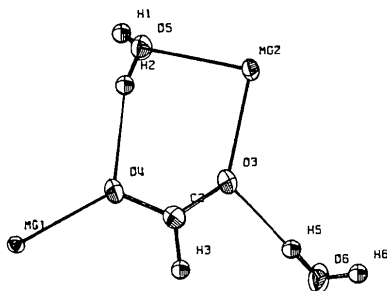


Fig. 4. Hydrogen bonding and coordination of formate ion (2).

different formate ions. The distances and angles found compare favourably with data on other formate ions [e.g. lithium formate, Enders-Beumer & Harkema (1973)].

Data pertaining to the geometry of the water molecules and the hydrogen bonds are given in Table 6. The first water molecule [O(5), H(1) and H(2)] is hydrogen bonded to O(2) and O(4). The other water molecule [O(6), H(5) and H(6)] also acts as a donor of two hydrogen bonds [O(1) and O(3)].

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Table 6. Bond distances (\AA) and angles ($^\circ$) related to the water molecules and the hydrogen bonds

	130 K	293 K
Water 1		
O(5)–H(1)	0.73 (3)	0.80 (2)
O(5)–H(2)	0.91 (3)	0.80 (3)
H(1)–O(5)–H(2)	106.9 (3.6)	107.4 (2.8)
O(5)–O(2)	2.774 (2)	2.794 (2)
O(5)–O(4)	2.762 (2)	2.814 (2)
Water 2		
O(6)–H(5)	0.92 (3)	0.83 (2)
O(6)–H(6)	0.78 (3)	0.81 (2)
H(5)–O(6)–H(6)	109.3 (3.4)	109.4 (2.7)
O(6)–O(1)	2.783 (2)	2.800 (2)
O(6)–O(3)	2.774 (2)	2.781 (2)

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