115·8°; as a result the C–C–O angles in the heterocycle are slightly larger than the trigonal angle and average 122·2°. The internal angles in the benzene rings are all very close to 120°. Repulsion between adjacent chlorine substituents may account for some opening of the C(2)–C(3)–Cl(3) and C(3)–C(2)–Cl(2) angles, which average 121·0°.

The chlorine atoms show large thermal amplitudes within the molecular plane and approximately perpendicular to the C–Cl bonds (Fig. 1). The oxygen atoms also display marked anisotropy, with the largest components directed approximately along the a axis or roughly normal to the molecular plane. The carbon atoms for the most part exhibit moderate anisotropy. Rigid-body analysis of the X-ray thermal parameters in 2,3,7,8-tetrachlorodibenzo-p-dioxin and some other chlorinated dioxins will be discussed elsewhere.

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The Molecular and Crystal Structure of KHCO3.MgCO3.4H2O

By GERHARD W. STEPHAN, CAROLINE H. MACGILLAVRY AND BEATRIX KOCH

Laboratory for Crystallography, University of Amsterdam, The Netherlands

KHCO3.MgCO3.4H2O is triclinic; $a = 6·713$, $b = 7·337$, $c = 5·364$ Å; $\alpha = 108·2$, $\beta = 108·9$, $\gamma = 59·6°$. Measured density $= 1·99$ g.cm^{-3}, $M = 256$, $Z = 1$. Space group possibly $P\bar{1}$. With K at 0,0,0, Mg is at 0,½,½. The Mg atom is in octahedral, the K atom in 12-fold oxygen surrounding. The two carbonate groups are centrosymmetrically arranged with the very short O···O distance of 2·42 Å. If the space group is indeed $P\bar{1}$ then the one acid hydrogen atom should be at the centre, ½,0,0, forming a symmetrical hydrogen bond.

During a vain attempt to synthesize the apparently extinct mineral lansfordite, MgCO3.5H2O, after the method of Menzel & Brückner (1930), colourless triclinic crystals were formed. Quantitative X-ray spectrometry showed a K content of $15·1 \pm 0·3$%, and a Mg content of $9·2 \pm 0·4$%. The carbonate content of a probably impure sample was determined by titration to be 37%. Cell constants were found from Weissen-berg zero-layer diagrams about three axes, with Cu $K\alpha$ radiation and calibrated with powder lines of Al.

$$a = 6·713 \ (3) \text{ Å} \qquad \alpha = 108·18 \ (3)°$$
$$b = 7·337 \ (3) \qquad \beta = 108·92 \ (3)$$
$$c = 5·364 \ (1) \qquad \gamma = \ 59·57 \ (2)$$

The density, determined by suspension, was 1·99 (1) g.cm^{-3}. This gives a cell formula weight of 256·4,

which together with the chemical analysis indicates one K^+, one Mg^{2+} and $1\cdot5$ CO_3^{2-} ions per cell. A value of $2CO_3^{2-}$ was considered more probable. The cell volume of $213\cdot6$ Å^3 is compatible with the presence of 10 oxygen atoms and one K^+ ion, if one assumes the volume per oxygen atom or K^+ ion to be 19 to 20 Å^3. To balance the charges, nine H^+ ions are then needed; this leads to the formula $KHCO_3.MgCO_3.4H_2O$. This has a formula weight of $256\cdot3$, which is in good agreement with the observed value.

Crystals of this composition are reported by Menzel & Brückner; they gave no crystallographic description but it can be assumed that these crystals are identical with the ones described above.

The crystals decompose when kept at temperatures above about $40\,^\circ C$. In a camera in which the powder diagram is registered at continuously varying temperature (Guinier–Lenné camera constructed by Nonius) the powder lines disappear completely at a temperature of about $50\,^\circ C$, indicating that the decomposed material is amorphous. After heating to $1100\,^\circ C$ and cooling to room temperature in contact with the atmosphere, the material shows the diffraction patterns of MgO and KOH.

A good single crystal was mounted on a Nonius single-crystal diffractometer. 860 independent reflexions were measured at room temperature, working with θ–2θ scan and Cu $K\alpha$ radiation. No absorption corrections were applied.

A Patterson synthesis indicated the single K and Mg atoms to be at a distance $0,\frac{1}{2},\frac{1}{2}$. The space group could

then well be $P\bar{1}$. A sphere in Patterson space of radius $R = 2\cdot95$ Å, the expected K–O distance, showed K to be surrounded by a cubic close packing of oxygen atoms, in agreement with the assumptions made during the derivation of the structural formula. The arrangement of O about K fits the octahedral surrounding of Mg which was derived from the Patterson function. C was also located in a position agreeing with the space group $P\bar{1}$ (see Fig. 1). The structure without H atoms was refined by a least-squares block-diagonal program and anisotropic temperature parameters to $R = 7\cdot5\%$. For eight very weakly observed reflexions, $|F_{obs}| < 2\cdot0$, the structure factor was calculated below the limit of perception. The five strongest reflexions, $|F_{calc}| > 40$, were observed to be somewhat less intense than expected, presumably due to extinction or to counting losses.

Atomic parameters are given in Table 1.

To our regret a difference Fourier synthesis gave no indication of hydrogen atomic positions. It may be that these do not conform to the space group $P\bar{1}$. They should be somewhere along the shortest O···O distances; these are indicated in Fig. 1. Among these, there is a remarkably short distance, $2\cdot42$ Å, across the (pseudo)centre at $\frac{1}{2},0,0$, between the two O(4) atoms of the mutually inverted CO_3 groups. This distance is in the range where symmetric hydrogen bonds have been found (Hamilton & Ibers, 1968). Therefore, a symmetric bond does seem possible, in agreement with $P\bar{1}$ symmetry. The deformation of the carbonate group is such as would be expected if O(4) bears half a hydrogen

Table 1. *Atomic coordinates and thermal parameters of* $KHCO_3.MgCO_3.4H_2O$

Standard deviations in brackets. Values $\times 10^5$, except for rational coordinates.

From the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{23}kl + 2\beta_{13}hl)]$ for anisotropic temperature movement.

	x	y	z	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{23}$	$2\beta_{13}$
K	0	0	0	842 (37)	1342 (34)	927 (49)	752 (59)	1091 (68)	194 (69)
Mg	0	$\frac{1}{2}$	$\frac{1}{2}$	−148 (42)	22 (35)	3143 (61)	160 (63)	273 (77)	−574 (83)
O(1)	1761 (46)	76172 (41)	45990 (62)	304 (75)	479 (64)	1686 (127)	−390 (115)	1490 (152)	−482 (160)
O(2)	26947 (42)	29602 (42)	29594 (56)	−115 (69)	611 (64)	570 (103)	276 (109)	409 (139)	−407 (139)
O(3)	76227 (44)	50856 (42)	13697 (55)	174 (75)	651 (68)	542 (107)	−104 (117)	354 (141)	−643 (146)
O(4)	61993 (45)	5489 (42)	20132 (55)	−96 (67)	518 (62)	539 (104)	44 (106)	−358 (134)	−477 (140)
O(5)	40394 (45)	75569 (45)	39312 (56)	142 (76)	1101 (75)	361 (105)	−523 (124)	−281 (148)	−446 (145)
C	49214 (57)	20197 (53)	37347 (74)	73 (93)	287 (78)	582 (137)	−329 (141)	674 (171)	−684 (179)

Table 2. *Some nearest neighbour distances and valence angles in* $KHCO_3.MgCO_3.4H_2O$
with their e.s.d.'s in brackets

K(0,0,0)–O(1) 2·910 (3) Å	Mg–O(1) 2·058 (4) Å	C–O(2) 1·275 (4) Å
K(0,0,1)–O(1) 3·363 (4)	Mg–O(2) 2·053 (3)	C–O(4) 1·309 (4)
K(0,0,0)–O(2) 3·269 (3)	Mg–O(3) 2·098 (3)	C–O(5) 1·266 (4)
K(0,0,0)–O(3) 3·175 (3)		
K(0,0,0)–O(4) 2·870 (4)		
K(0,0,0)–O(5) 2·967 (3)		

O(1)–Mg–O(2) 90·94 (13)°   O(2)–C–O(4) 118·0 (5)°
O(2)–Mg–O(3) 91·64 (10)°   O(4)–C–O(5) 118·3 (5)°
O(3)–Mg–O(1) 91·64 (13)°   O(5)–C–O(2) 123·5 (5)°

O(1)H···O(4) = 2·71 Å   O(3)H···O(2) 2·97 Å   O(4)···H···O(4') 2·42 Å
O(1)H···O(5) = 2·70 Å   O(3)H···O(5) 2·67 Å

atom. The odd H atom would then be located in special position at $\frac{1}{2},0,0$.

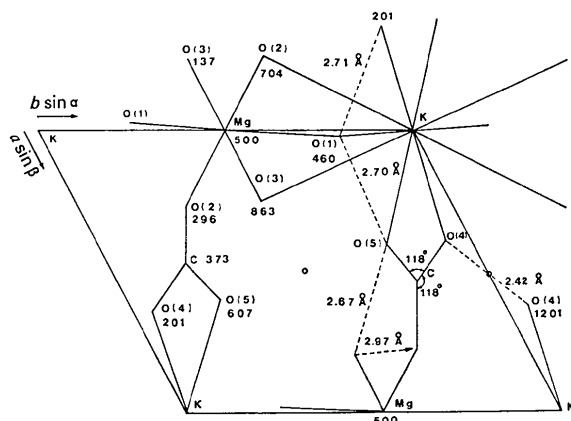K at 0,0,0 is surrounded by four atoms O(1), and two of each of the oxygen atoms O(2), O(3), O(4) and O(5). Its

Fig. 1. The crystal structure of $KHCO_3.MgCO_3.4H_2O$ projected along the c axis; z coordinates are given in fractions multiplied by 1000. Probable hydrogen bonds are marked with dotted lines.

polyhedron shares edges O(1)–O(1') with the K ions at 0,0,1 and 0,0,$\bar{1}$, and edges O(2)–O(3) with Mg ions at $0,\frac{1}{2},\frac{1}{2}$ and $0,-\frac{1}{2},-\frac{1}{2}$. It links the carbonate groups in subsequent cells along the c axis through O(4) in the cell below and O(5) in the cell shown in the Figure.

A list of calculated and observed structure factors is available upon request from the Laboratory for Crystallography of the University of Amsterdam, 126 Nieuwe Prinsengracht, Amsterdam C, Netherlands. Interatomic distances are given in Table 2.

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The Crystal Structure of Nesquehonite, $MgCO_3.3H_2O$

BY G. W. STEPHAN AND CAROLINE H. MACGILLAVRY

Laboratory for Crystallography, University of Amsterdam, Netherlands

Nesquehonite is monoclinic; $a = 7.705$, $b = 5.367$, $c = 12.121$ Å, $\beta = 90°.45$. Space group $P2_1/n$, $Z = 4$. The Mg ions are surrounded by strongly deformed oxygen octahedra, sharing an edge with a carbonate group, and a corner with another Mg octahedron. This leads to infinite strings along the b axis.

The crystal structure of nesquehonite was studied about 20 years ago (Kinsolving, MacGillavry & Pepinsky, 1950). It was then established that all available crystals are strongly twinned on (001); resolution of the two orientations was obtained by means of a specially constructed Weissenberg camera with a ratio of film-holder shift to crystal rotation twice as large as usual. Although a trial structure was set up at the time, no information about this was given in the short communication referred to above. Correspondence with Professor Pepinsky revealed that the old data could not easily be traced. In view of our general interest in hydrated magnesium carbonates we decided, with Pepinsky's permission, to take up the structure determination again.

Crystals of nesquehonite were prepared synthetically by the method of Menzel & Brückner (1930). Clear, thin needles were obtained of a size suitable for structure determination. Among these needles we never found an untwinned specimen, so we had to work with what was probably a multiple twin.

Cell constants

These were determined from Weissenberg diagrams $h0l$ and $hk0$, taken with Cu $K\alpha$ radiation and calibrated with Al powder lines. They agree with the older data:

Present results	Kinsolving *et al.*
$a = 7.7053$ (11) Å	$a = 7.68$ Å
$b = 5.3673$ (6)	$b = 5.39$
$c = 12.1212$ (11)	$c = 12.00$
$\beta = 90.451$ (13)°	$\beta = 90.45°$

$Z = 4$, X-ray density 1·85 g.cm^{-3}. The needles are elongated along the b axis. Space group $P2_1/n$.

Intensities of reflexions

Owing to the twinning low θ reflexions hkl and $hk\bar{l}$ coincide; at higher θ the deviation of β from 90° is