Table 1. *Indices and the calculated moduli of the reciprocal vector* **g** *and Bragg angles* θ *of HOLZ lines shown in Figs.* 2 *and* 3

	s.i. Al–Mn–Si								f.c.i. Al–Cu–Fe							
Line No.	n_1^*	n_2^*	n_3^*	n_4^*	n_5^*	n_6^*	g	θ (°)	n_1^*	n_2^*	n_3^*	n_4^*	n_5^*	n_6^*	g	θ (°)
1	−1	−1	−4	−2	2	3	0·9086	0·9610	−2	−2	−8	−4	4	6	0·9323	0·9861
2	−2	−4	−1	2	1	−3	0·9086	0·9610	−4	−8	−2	4	2	−6	0·9323	0·9861
3	2	3	4	1	−2	−1	0·9086	0·9610	4	6	8	2	−4	−2	0·9323	0·9861
4	−1	−2	1	2	0	−3	0·6681	0·7066	−2	−4	2	4	0	−6	0·6855	0·7251
5	0	1	−2	−2	1	3	0·6681	0·7066	0	2	−4	−4	2	6	0·6855	0·7251
6	−3	−5	−5	0	3	0	1·2675	1·3405	−6	−10	−10	0	6	0	1·3005	1·3755
7	3	5	3	−1	−2	2	1·1078	1·1717	6	10	6	−2	−4	4	1·1367	1·2022
8									3	3	5	1	−3	−1	0·6572	0·6950

Table 2. *Comparison of the measured values of the quasilattice parameters*

	s.i. $Al_{76}Si_4Mn_{20}$	f.c.i. $Al_{65}Cu_{20}Fe_{15}$		
	Elser (1985) and Bancel *et al.* (1985)	Tsai *et al.* (1987)	Ebalard & Spaepen (1989)	This work
Indices	211111	100000	1888888	422222
$2\pi g$ (nm^{-1})	28·96	29·76	29·8	
a (nm)	0·4595	$0·894_2$	$0·893_2$	
Indices	221001	110000	1610001016	442002
$2\pi g$ (nm^{-1})	30·43	31·41	31·3	
a (nm)	0·4598	$0·891_0$	$0·894_1$	
Averaged a (nm)	0·4597	$0·892_6$	$0·893_6$	$0·896_6$

inflation factors of $\tau^{-3}/2$ and τ^3, respectively, with $\tau = (\sqrt{5} + 1)/2$ the golden mean. When quasilattice parameters for f.c.i. $Al_{65}Cu_{20}Fe_{15}$ are reduced to the s.i. lattice (divided by a factor of two) they become about 2·5% smaller than those of s.i. $Al_{76}Si_4Mn_{20}$. Noticing that the values of the atomic radii are 1·43, 1·17, 1·12, 1·28 and 1·28 Å for Al, Si, Mn, Cu and Fe, respectively (Wood, 1971), the mean atomic radii for $Al_{76}Si_4Mn_{20}$, $Al_{65}Cu_{20}Fe_{15}$ and $Al_{63}Cu_{24}Fe_{13}$ are 1·36, 1·38 and 1·37 Å, respectively. Therefore, this difference of 2·5% cannot be explained by the difference in the mean atomic radii. A possible explanation may be an ordering effect which may induce a shrinkage of the quasilattice.

We would like to thank Professor F. H. Li, Dr M. J. Hui and Dr Y. F. Cheng of the Institute of Physics, Academia Sinica, for providing the specimen of $Al_{65}Cu_{20}Fe_{15}$ and for sending us their unpublished research report.

References

Bancel, P. A., Heiney, P. A., Stephens, P. W., Goldman, A. I. & Horn, P. M. (1985). *Phys. Rev. Lett.* **54**, 2422–2425.

Dai, M. & Wang, R. (1990). *Solid State Commun.* **73**, 77–80.

Ebalard, S. & Spaepen, F. (1989). *J. Mater. Res.* **4**, 39–43.

Ecob, R. C., Shaw, M. P., Porter, A. J. & Ralph, B. (1981). *Philos. Mag. A*, **44**, 1117–1133.

Elser, V. (1985). *Phys. Rev. B*, **32**, 4892–4898.

Jones, P. M., Rackham, G. M. & Steeds, J. W. (1977). *Proc. R. Soc. London Ser. A*, **354**, 197–222.

Shindo, D., Hiraga, K., Williams, T., Hirabayashi, M., Inoue, A. & Masumoto, T. (1989). *Jpn. J. Appl. Phys.* **28**, L688–L689.

Tsai, A. P., Inoue, A. & Masumoto, T. (1987). *Jpn. J. Appl. Phys.* **26**, L1505–L1507.

Wang, R., Zou, H. & Jiao, S. (1986). *Proc. 11th Int. Congr. Electron Microscopy*, Kyoto, pp. 711–712.

Wood, W. A. (1971). *The Study of Metal Structures and Their Mechanical Properties*, p. 369. New York: Pergamon Press.

Acta Cryst. (1990). **B46**, 458–466

Structure and Electron Density of Nickel Potassium Hydrogenbiscarbonate Tetrahydrate

By Nelson G. Fernandes,[*] Roland Tellgren and Ivar Olovsson

Institute of Chemistry, University of Uppsala, Box 531, *S*-751 21 *Uppsala, Sweden*

(*Received* 4 *December* 1989; *accepted* 14 *February* 1990)

Abstract

$KNiH(CO_3)_2.4H_2O$, $M_r = 290·7$, triclinic, $P\bar{1}$, $a = 5·3824$ (2), $b = 6·6737$ (2), $c = 6·9480$ (2) Å, $\alpha = 115·881$ (2), $\beta = 90·678$ (2), $\gamma = 108·017$ (2)°, $V = 210·37$ (1) Å^3, $Z = 1$, $D_x = 2·31$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 2·859$ mm^{-1}, $F(000) = 148$, $T = 298$ K, $R(F^2) = 0·0350$ for 5228 unique reflections. Two carbonate groups are linked by a short hydrogen bond, with an O···O distance of 2·456 (2) Å, forming a nearly planar centrosymmetric anion, $[H(CO_3)_2]^{3-}$. The non-spherical distribution of the

---

[*] Permanent address: Department of Chemistry, Federal University of Minas Gerais, CP 702, 30161 Belo Horizonte, Brazil.

0108-7681/90/040458-09$03.00

valence electrons was taken into account by deformation density refinements (Hirshfeld procedure). The deformation density maps are in good agreement with other experimental and theoretical studies.

Introduction

This work is part of a series of structure investigations of hydrogen carbonates. In the structure of $KMgH(CO_3)_2.4H_2O$ (Fernandes, Tellgren & Olovsson, 1988) two carbonate groups are linked by a short, crystallographically symmetric hydrogen bond of 2·46 Å to form an $H(CO_3)_2^{3-}$ ion. The proton appears to be disordered at room temperature but located at the centre of symmetry at low temperature.

The object of the present investigation of the closely related Ni compound was to study the electron density in the short hydrogen bond and in the water molecules. Furthermore, this compound is a good candidate for studying the details of the electron distribution around the Ni ion. Special care was therefore taken in the data collection, which was extended to the highest possible resolution.

Experimental

$KNiH(CO_3)_2.4H_2O$ was prepared in a similar way to $KMgH(CO_3)_2.4H_2O$ (Fernandes, Tellgren & Olovsson, 1988). A detailed description of the concentration range in which these compounds are formed has been reported by Nanty (1912, 1913) who also synthesized $KCoH(CO_3)_2.4H_2O$. The best crystals were obtained by adding, drop by drop, 0·50 g $NiCl_2.6H_2O$ dissolved in 2 ml water to 7·00 g $KHCO_3$ dissolved in 50 ml water at room temperature, followed by slow evaporation. After 2–3 days small green well-shaped crystals were formed, most of them twins; the crystals were examined by polarizing microscope and Weissenberg techniques. A single crystal of size 0·05 × 0·10 × 0·22 mm was used for the data collection on an automated Stoe–Philips four-circle diffractometer, graphite monochromator, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å. Unit-cell parameters were determined from 77 reflections in the range $20 \leq 2\theta \leq 30°$. Although the Ni compound has a structure similar to the Mg compound, it was necessary to choose the unit cell differently in order to follow the conditions for defining a reduced basis given in the *International Tables for Crystallography* (1983).

The intensity measurements were made in the ω–2θ scan mode, step width in ω equal to 0·015° with a minimum number of 96 steps plus the $K\alpha_1 - K\alpha_2$ splitting, at rate ranging from 0·8–3·2 s step^{-1}; attenuation filters were used. Five standard reflections of different intensities were measured at 4 h intervals: no systematic intensity variation was observed throughout the experiment, the maximum intensity variation being less than 3% from the mean value. All reflections within a full reciprocal-lattice sphere of radius $(\sin\theta)/\lambda \leq 0{\cdot}900$ Å^{-1} and a hemisphere of radius $0{\cdot}900 < (\sin\theta)/\lambda \leq 1{\cdot}146$ Å^{-1}, corresponding to $-12 \leq h \leq 12$, $-15 \leq k \leq 15$, $-16 \leq l \leq 16$, were measured at 295 K; 10180 reflections in total, including 1265 repeated standard reflections. The data were corrected for background effects by the Lehmann & Larsen (1974) profile analysis method, and for Lorentz, polarization and absorption effects (transmission factors 0·624–0·875). This resulted in 5228 unique reflections, $R_{\text{int}} = \sum|I - \langle I\rangle|/\sum I = 0{\cdot}0071$ where $\langle I\rangle$ is the weighted mean. The variance of an averaged reflection was chosen to be the larger of $V_1 = [\sum w_i(I_i - \langle I\rangle)^2]/\sum w_i$ or $V_2 = \sum\sigma_i^2/n$, where $w_i = 1/\sigma_i^2$ and σ_i^2 is the variance due to counting statistics and the corrections cited above; n is the number of averaged reflections. The inverse of V_1 (or V_2) was used as weight in the least-squares refinements.

Table 1. *Details of the refinements*

A, free-atom model refinement. *B*, deformation refinement, 63 refined deformation parameters. $\Delta = |F_o|^2 - |F_c|^2$, $\sigma = \sigma(F_o^2)$, $w = 1/\sigma^2$, $(\sin\theta/\lambda)_{\max} = 1{\cdot}1461$ Å^{-1}, n (number of observations) = 5228.

	A	*B*
k (scale factor × F_o)	1·6572 (9)	1·6381 (35)
p (number of refined parameters)	84	142
$R = \sum\|\Delta\|/\sum F_o^2$	0·0429	0·0350
$wR = (\sum w\Delta^2/\sum wF_o^4)^{1/2}$	0·0425	0·0312
$S = [\sum w\Delta^2/(n-p)]^{1/2}$	1·431	1·055
Number of reflections with $\|\Delta\| > 4{\cdot}0\sigma$	80	5
Ratio of maximum least-squares shift to e.s.d. in final refinement cycle	$1{\cdot}5 \times 10^{-3}$	$0{\cdot}8 \times 10^{-3}$
Minimum and maximum heights in difference maps (e Å^{-3})	−1·35, 2·47	−0·88, 0·68

Conventional refinements

Patterson synthesis gave the Ni and K positions; O and C atoms were located from a subsequent Fourier synthesis, H atoms from $\Delta\rho$ maps. Neutral-atom scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). Refinement was by full-matrix least-squares methods using all 5228 unique reflections. The function minimized was $\sum w(F_o^2 - k^2F_c^2)^2$. A total of 84 parameters were refined: one scale factor, 30 positional, 48 anisotropic thermal parameters, and five isotropic thermal parameters for H atoms. The details of the refinement are given in Table 1. The programs used for all computations have been described by Lundgren (1982). Stereoscopic illustrations were drawn using *ORTEP*II (Johnson, 1976). Least-squares refinements of models with isotropic extinction: (i) type I, (ii) type II, according to Becker & Coppens (1974, 1975) resulted in slightly negative extinction coefficients, which indicated that extinction corrections could be neglected.

Refinements of third-order tensors for temperature factors corresponding to both Edgeworth and Gram–Charlier expansions of probability functions were also undertaken (*International Tables for X-ray Crystallography*, 1974, §5.2.3). The inclusion of 80 parameters for the γ tensors in the refinement did not drop wR significantly at the 0·005 level (Hamilton, 1965) by using the Edgeworth expansion. In contrast, a significant improvement was noticed in wR at the 0·005 level by using the Gram–Charlier expansion. However, in both cases the R values were approximately equal to the value reported in refinement A in Table 1, and the parameters agreed within one estimated standard deviation. It was thus concluded that the atomic vibrations for non-H atoms could be reasonably described in a harmonic potential field with a Gaussian probability density function.

Deformation refinements

Following the Hirshfeld (1971, 1977) procedure, to each spherical scattering factor f_s a set of functions φ_l was added which take into account the non-spherical distribution of the valence electrons around the atomic nuclei, such that the total scattering factor, f, for an atom is given by

$$f = f_s + \sum c_l \varphi_l$$

where φ_l are the Fourier transforms of the deformation density functions ρ centred on each atom. In the Hirshfeld method, the functions for expanding the deformation density are related to the spherical harmonics and are of the general form

$$\rho_n(r_a, \theta_k) = N_n r_a^n \exp(-\alpha_a r_a) \cos^n \theta_k$$

where n is an integer between 0 and 4, r_a is the distance of a point from the nucleus a, θ_k is the angle between the vector r_a and a specified polar axis k, α_a is a parameter that governs the radial breadth of the deformation functions on each type of atom, and N_n is a normalizing constant. For n up to 4, it is possible to specify 35 deformation functions for each atom and to refine the coefficients c_l plus the α_a value for each type of atom. Functions for $n \leq 2$ were used for the H atom in the short hydrogen bond; $n \leq 3$ for the H atoms of the water molecules, C and O; $n \leq 4$ for K and Ni. In order to reduce the number of refinable parameters, symmetry and chemical constraints were imposed. The local symmetry assigned to each atom was: 'spherical' for K; 'axial' for any H atoms along the O—H bond; $m\bar{3}m$ for Ni; $mm2$ for O1, O2, O3, O4 and C. For the water molecule, the twofold axis was chosen in the molecular plane and bisecting the H—O—H angle; for O3 and O4 the twofold axis coincides with the C—O bond; for C it coincides with the C—O5 bond; m for O5 is in the C—O5—H5 plane. With these symmetry constraints the two H atoms in each water molecule share the same deformation coefficients as do O3 and O4 in the hydrogenbiscarbonate group. The electron densities for the two water molecules in the asymmetric unit were assumed to be equivalent. Thus the number of deformation atom types was eight. It is well known that the H position determined by X-ray diffraction is shifted towards the heavy atom compared with the nuclear position determined by neutron diffraction, see for example, Olovsson & Jönsson (1976). Therefore the positions of the H atoms in the water molecules derived from refinement A were corrected to give an O—H distance of 0·963 Å and an H—O—H angle of 107°, which are the average values tabulated by Chiari & Ferraris (1982) for the water molecule in a series of crystalline hydrates studied by neutron diffraction. In the absence of neutron and spectroscopic data, the isotropic thermal parameters B_{iso} were arbitrarily fixed to 3·3 Å^2 for all H atoms. The coefficients c_0 of the cusp function ($\rho_{n=0}$) were fixed to zero for all non-H atoms. With these assumptions, the model had 122 parameters to be refined: one scale factor, 66 positional and anisotropic thermal parameters, 45 deformation coefficients c_l and eight α values. After convergence was reached, the next step was to refine the cusp functions for the heavy atoms and the water H-atom positions. However, this refinement diverged if the cusp function for K was also refined. Hence α_K was fixed at the value of the refinement described above and the number of parameters refined increased to 139. The validity of the symmetry and the chemical constraints were subsequently checked. The symmetry on the Ni site was lowered from $m\bar{3}m$ to $4/mmm$, which meant an addition of three refined parameters. With the Ni—O3 direction lying on the unique axis, R and wR dropped significantly and the shape of the deformation map around Ni changed substantially.

The symmetry on the Ni site was now lowered to mmm. It left the deformation map around Ni invariant and did not lead to a significant drop in R and wR. Consequently, for this experiment, the most adequate choice of symmetry for the Ni site is $4/mmm$, with Ni—O3 as the unique axis.

Relaxation of the symmetry and chemical constraints for any other atom and inclusion of functions with exponent $n = 4$ on C and O atoms led to a non-significant improvement in R and wR. Hence these refinements will not be considered. The final deformation refinement B in Table 1 has all the initial symmetry and chemical constraints, except for the Ni site which was relaxed to $4/mmm$ as mentioned above. From Table 1 it can be seen that a model which takes into account the non-spherical distribution of the valence electrons is better than a

Table 2. *Atomic coordinates and equivalent isotropic thermal parameters* ($Å^2 \times 10^2$) *from the deformation refinement*

For non-H atoms, $\langle u^2 \rangle = (1/6\pi^2)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$\langle u^2 \rangle$
Ni	0·50000	0·50000	0·50000	1·074 (8)
K	0·00000	0·00000	0·00000	2·770 (8)
O1	0·53498 (11)	0·21697 (8)	0·23439 (7)	1·974 (14)
O2	0·86257 (8)	0·73080 (6)	0·49659 (11)	1·923 (13)
O3	0·28775 (8)	0·55872 (9)	0·29576 (7)	1·817 (17)
O4	0·60638 (14)	0·83920 (10)	0·25084 (7)	2·194 (17)
O5	0·20226 (26)	0·67491 (20)	0·05540 (16)	1·926 (23)
C	0·37233 (15)	0·69139 (7)	0·20511 (13)	1·407 (16)
H1	0·658 (4)	0·259 (2)	0·114 (4)	4·2*
H1†	0·621 (2)	0·251 (2)	0·148 (2)	1·2 (2)
H2	0·588 (2)	0·073 (4)	0·253 (2)	4·2*
H2†	0·572 (2)	0·115 (2)	0·248 (2)	1·5 (2)
H3	1·011 (5)	0·651 (3)	0·411 (3)	4·2*
H3†	0·970 (2)	0·671 (2)	0·438 (2)	1·5 (2)
H4	0·801 (3)	0·804 (3)	0·393 (3)	4·2*
H4†	0·811 (3)	0·785 (2)	0·421 (2)	3·0 (4)
H5	0·000	0·500	0·000	4·2*
H5†				6·9 (8)

* Hydrogen thermal parameters not refined, see text.

† Refined hydrogen parameters derived from the free-atom model.

Table 3. *Selected interatomic distances* (Å) *and angles* (°) *from the deformation refinement*

(*a*) Ni ion			
O1—Ni—O2	92·47 (2)	O2—Ni—O3	86·06 (2)
O1—Ni—O3	88·67 (2)		
(*b*) Carbonate group, water molecules and hydrogen bonds			
C—O3	1·278 (1)	O3—C—O4	124·54 (7)
C—O4	1·269 (1)	O3—C—O5	117·42 (8)
C—O5	1·322 (1)	O4—C—O5	118·03 (8)
O1—H1	1·15 (2)		
O1—H2	1·14 (3)	H1—O1—H2	107 (1)
O1···O5	2·698 (1)	O1—H1···O5	173 (2)
O1···O4	2·714 (1)	O1—H2···O4	169 (1)
O2—H3	1·13 (2)		
O2—H4	1·13 (2)	H3—O2—H4	104 (1)
O2···O3	2·947 (1)	O2—H3···O3	172 (2)
O2···O4	2·642 (1)	O2—H4···O4	157 (1)
O5···H5	1·228 (1)		
O5···O5′	2·456 (2)		

model which disregards this feature. The positional and equivalent isotropic displacement parameters are shown in Table 2.*

Description of the structure

Interatomic distances and bond angles are given in Table 3. The structure illustrated in Fig. 1 is closely similar to the Mg compound (Fernandes, Tellgren & Olovsson, 1988). The Ni ion is octahedrally surrounded by six O atoms; the K ion has twelve O neighbours in a nearly close-packed arrangement, Fig. 2. The water O2 atom has a tetrahedral coordination whereas the water O1 atom has an unusual coordination with five neighbours. The bonding situation of the water molecules is shown in Fig. 2 of the earlier paper on the Mg compound.

Two carbonate ions are linked by a short hydrogen bond, O···O distance 2·456 (2) Å, forming a slightly twisted $H(CO_3)_2^{3-}$ ion with a centre of symmetry in the middle of the hydrogen bond. The atoms in the carbonate group deviate by less than 0·0044 (8) Å from the least-squares plane through the four atoms. A three-dimensional network of hydrogen bonds is formed between the $H(CO_3)_2^{3-}$ ions and the water molecules (Fig. 1). The atomic arrangement in the corresponding Mg compound (Fernandes, Tellgren & Olovsson, 1988) is closely similar.

In the present refinement the H atom in the $H(CO_3)_2^{3-}$ ion is located at the centre of symmetry. There is no apparent disorder, *e.g.* two closely spaced electron density peaks around the centre of symmetry. The situation was more complicated in the Mg compound: at room temperature two peaks appeared around the centre of symmetry but only one peak at low temperature. The present results are

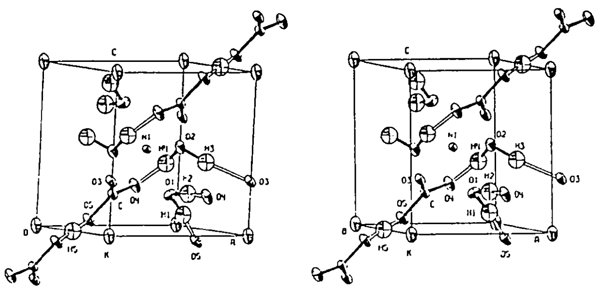


Fig. 1. Steroscopic view of the structure of $KNiH(CO_3)_2.4H_2O$. Here and in the following figures the thermal vibration ellipsoids are drawn to include 50% probability (results from the deformation refinement).

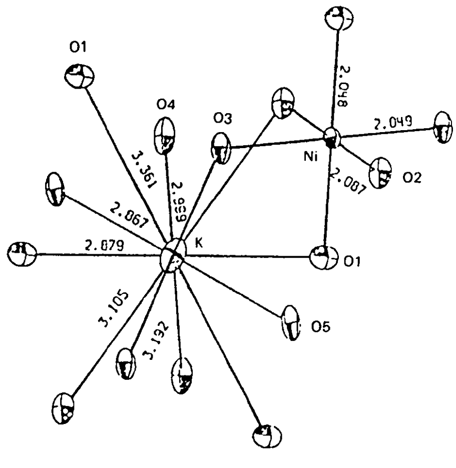


Fig. 2. Coordination around K and Ni ions in $KNiH(CO_3)_2.4H_2O$ (results from the deformation refinement).

---

* Lists of structure factors, deformation coefficients and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52740 (48 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

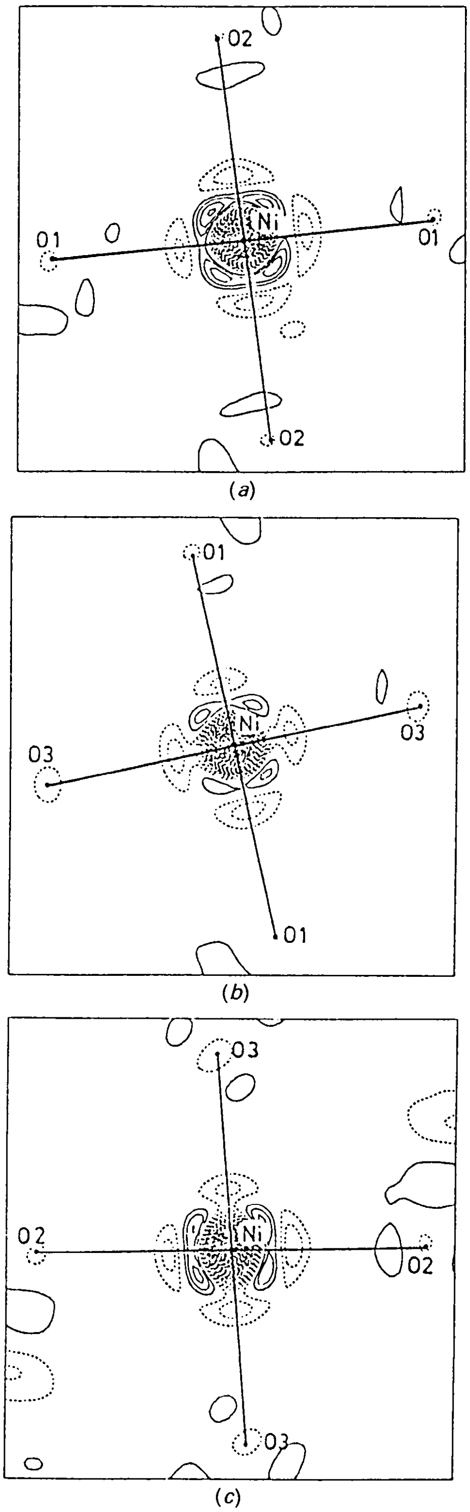


Fig. 3. Dynamic deformation density around the Ni atom in $KNiH(CO_3)_2.4H_2O$. Contours are plotted at 0·20 e Å^{-3} intervals. Solid and dashed lines denote positive and negative contours respectively; the zero level has been omitted: (*a*) Ni—O1—O2 plane; (*b*) Ni—O1—O3 plane; (*c*) Ni—O2—O3 plane.

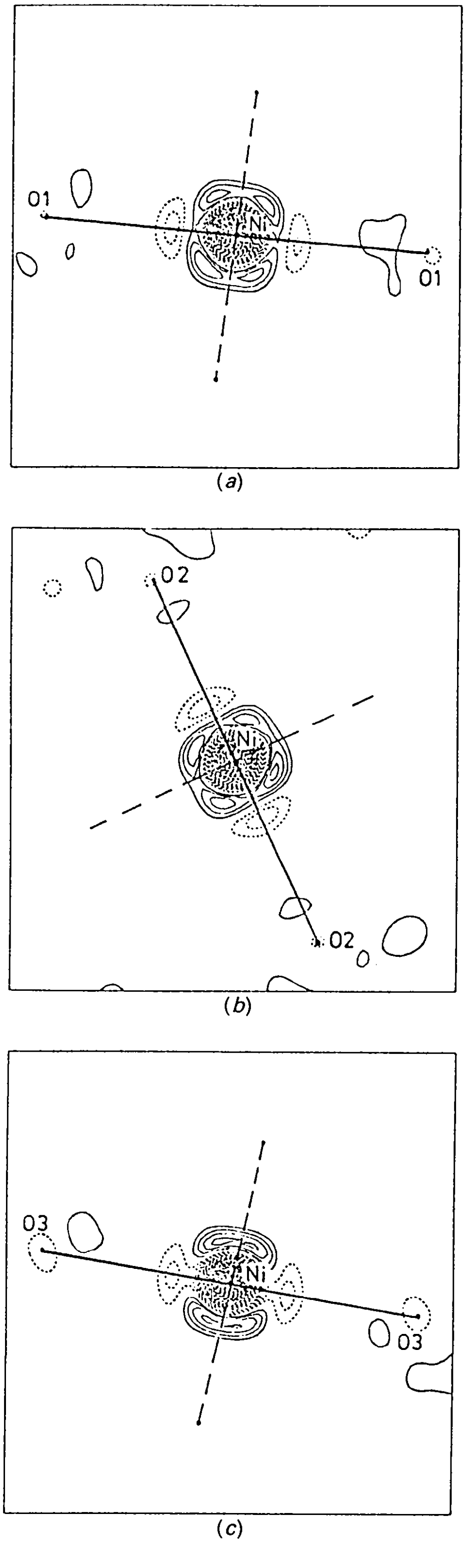


Fig. 4. (*a*)–(*c*) Dynamic deformation density around the Ni atom in $KNiH(CO_3)_2.4H_2O$. The planes are defined by a line joining the Ni atom with one O atom (shown in the figures) and a line (dashed) bisecting the angle between the Ni atom and two of the equatorial O atoms. Contours as in Fig. 3.

thus similar to the situation at low temperature in the Mg compound. The O···O bond distance is similar in the two compounds, 2·456 (2) and 2·461 (3) Å, respectively, at room temperature. The deformation electron density in the short hydrogen bond and around the carbonate and Ni ions is discussed in the next section.

Deformation density maps

The Ni *ion*

Figs. 3 and 4 show the deformation density around Ni. There is an electron deficiency in the Ni—O bonds at ~0·60 Å from the Ni nucleus but an electron excess of 0·60–0·80 e Å^{-3} between the Ni–ligand directions at ~0·45 Å from the metal nucleus. Ni^{2+} has a d^8 electron configuration and in the present case Ni is almost regularly octahedrally surrounded by six O atoms (four water molecules and two carbonate groups). The simplest version of ligand-field theory predicts an electron configuration $t_{2g}^6e_g^2$ with a preferential occupation of the t_{2g} orbitals directed between the ligands as compared to the e_g orbitals along the metal–ligand axes. This corresponds to an electron deficiency along the Ni—O bonds as compared to the diagonal directions in complete agreement with the present experimental observations. Similar results have been obtained in, for example, FeS_2 (Stevens, DeLucia & Coppens, 1980), $K_2Na[Co(NO_2)_6]$ (Ohba, Toriumi, Sato & Saito, 1978), $Ni(NH_3)_4(NO_2)_2$ (Figgis, Reynolds &

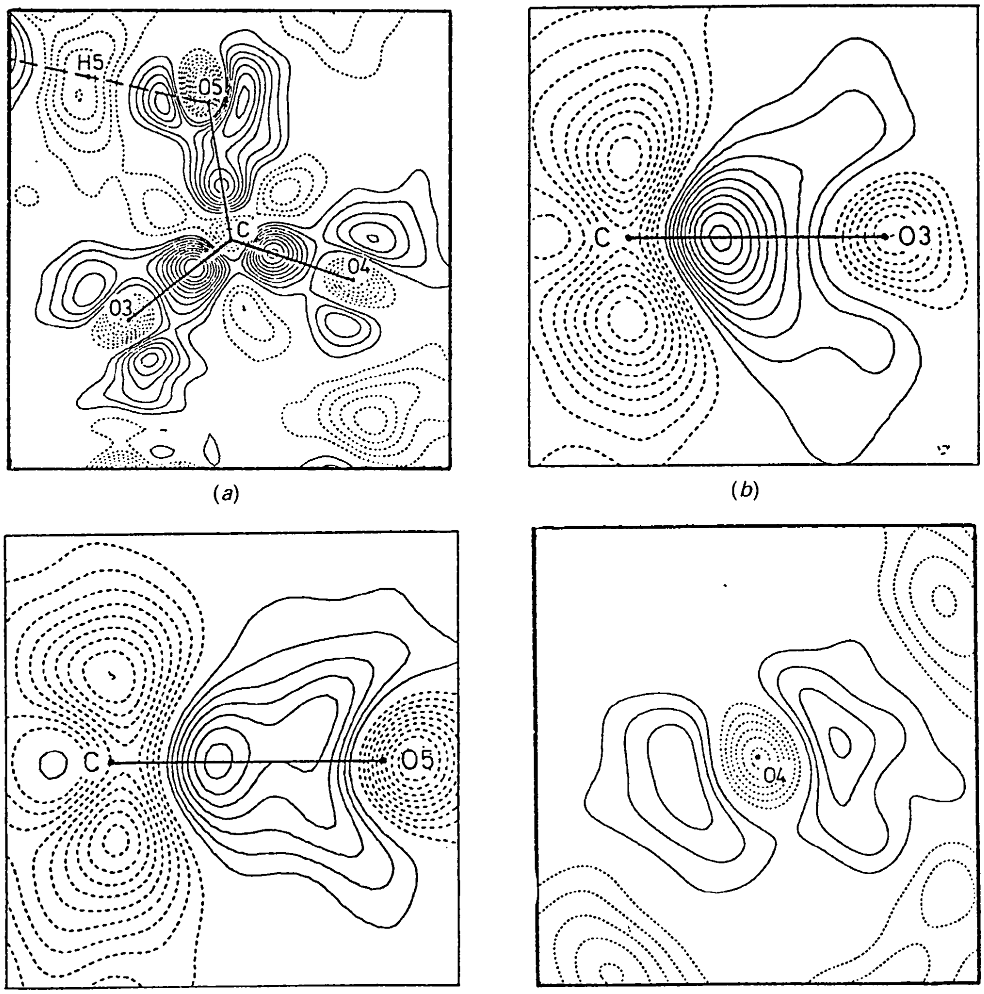


Fig. 5. Dynamic deformation density in some sections through the carbonate group in $KNiH(CO_3)_2.4H_2O$: (*a*) least-squares plane through the atoms C, O3, O4 and O5; (*b*) plane perpendicular to the plane defined in (*a*) containing the C—O3 bond; (*c*) plane perpendicular to the plane defined in (*a*) containing the C—O5 bond; (*d*) plane perpendicular to the C—O4 bond, 0·1 Å behind the O atom. Contours here and in the following figures are at intervals of 0·05 e Å^{-3}. Solid lines and dashed lines denote positive and negative contours respectively; the zero level has been omitted.

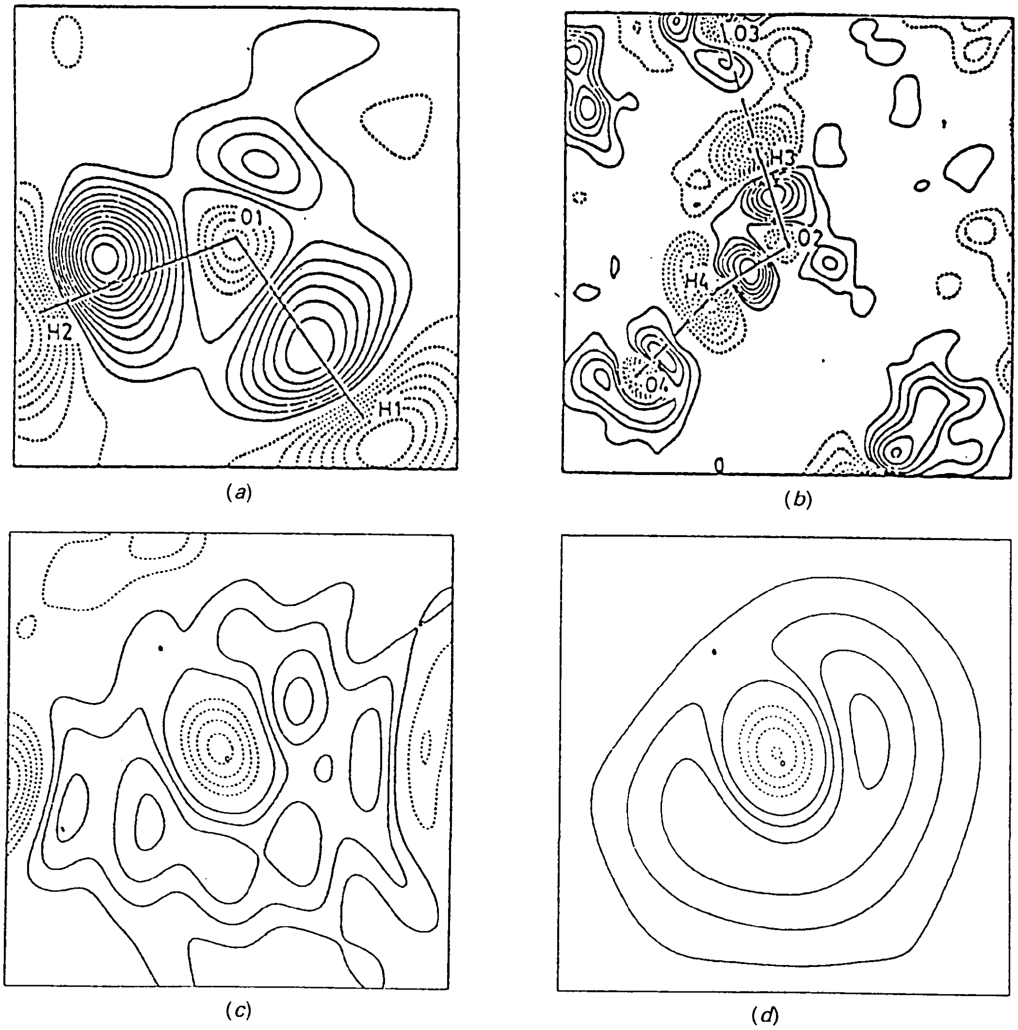
Wright, 1983) and $NiSO_4.6D_2O$ (McIntyre, Ptasiewicz-Bak & Olovsson, 1990).

The carbonate group

Density maps in the carbonate plane and some other sections are shown in Fig. 5. The different bonding situation for the three O atoms can be clearly seen. The maximum peak heights in the C—O3 and C—O4 bonds are 0·55 and 0·50 e Å^{-3}, respectively, whereas the maximum height in the C—O5 bond is only 0·30 e Å^{-3}, reflecting the difference between a delocalized double bond and a single bond. The lone-pair regions around the O atoms differ as well. Two very similar density regions, as expected for a situation close to sp^2 hybridization, can be seen on both sides of O3 and O4. The electron distribution around O5 on the other hand is closer to an sp^3 hybrid. The overall features in the bonding and non-bonding regions in the carbonate groups are similar to those found in carboxylate groups, as, for example, in NaHCOO (Fuess, Bats, Dannöhl, Meyer & Schweig, 1982), α-$Ca(HCOO)_2$ (Fuess, Burger & Bats, 1981) and $NaHC_2O_4.H_2O$ (Delaplane, Tellgren & Olovsson, 1990).

The water molecules

The deformation densities in some sections involving the water molecules are shown in Fig. 6. The maps in the planes of the two water molecules, Figs. 6(*a*) and 6(*b*), have the usual characteristic features (O—H bond peak ~0·40 e Å^{-3}). They are



(*a*) (*b*)

(*c*) (*d*)

Fig. 6. Dynamic deformation density in sections through the water molecules in $KNiH(CO_3)_2.4H_2O$: (*a*) plane defined by H1—O1—H2; (*b*) least-squares plane through O3, H3, O2, H4 and O4, contours as in Fig. 5; (*c*) plane perpendicular to the plane of the water molecule (2) and bisecting the H3—O2—H4 angle; (*d*) plane as in (*c*) but with only deformation functions centred on the water molecule included.

very similar, as expected, since chemical equivalence was assumed in the deformation model. However, as the thermal smearing is included in the calculation they do not have to be identical. The density in the plane perpendicular to the plane of the water molecule (2) and bisecting the H—O—H angle is shown in Fig. 6(*c*). As typically observed for water molecules there are not two pronounced lone-pair maxima but a very broad density distribution throughout the whole lone-pair region; *cf.* for instance $NaHC_2O_4.H_2O$ (Delaplane, Tellgren & Olovsson, 1990).

The influence of the neighbours on the electron density has been discussed earlier (Olovsson, 1980). In the paper on $NiSO_4.6D_2O$ (McIntyre, Ptasiewicz-Bak & Olovsson, 1990) the effect of the simple superposition of the density contours of adjacent molecules was discussed in some detail. It was pointed out, for instance, that superposition of electron densities from adjacent molecules may lead to a considerable modification of the contours in the lone-pair region of the water molecules. In order to study this superposition effect, maps were calculated where only the deformation functions centred on the water molecules were included. The resulting 'partial deformation density map' corresponding to Fig. 6(*c*) is shown in Fig. 6(*d*). The contours are now much smoother and in favourable qualitative agreement with theoretical calculations (Hermansson, 1987). Noteworthy is a small peak in the direction of the Ni ion and this is possibly due to the polarizing effect of the metal ion. The corresponding maps in the planes of the water molecules show a similar smoothing effect but are not significantly different from those shown in Figs. 6(*a*) and 6(*b*).

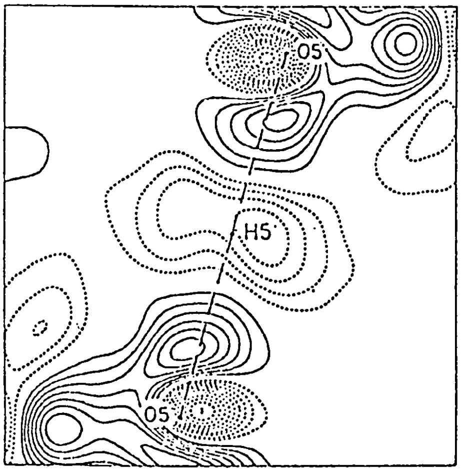


Fig. 7. Dynamic deformation density in a plane defined by the atoms in the O5···H5···O5′ hydrogen bond and a C atom in $KNiH(CO_3)_2.4H_2O$. Contours as in Fig. 5.

The hydrogen bonds

The hydrogen bonds involving the water molecules range from 2·64 to 2·95 Å (Table 3). The deformation densities exhibit peaks and troughs characteristic for hydrogen bonds in this range, as illustrated for water molecule (2) in Fig. 6(*b*).

The deformation density in the very short symmetric hydrogen bond of 2·456 (2) Å is shown in Fig. 7. A peak is observed between the O atom and the inversion centre, whereas an ellipsoidal trough is found around the inversion centre. This could perhaps be interpreted as a consequence of symmetry. However, theoretical calculations (Hermansson, 1987) predict a trough in the middle of the hydrogen bond as the O···O distance decreases. In fact, Fig. 7 compares qualitatively well with the static theoretical deformation density (crystal field included) of the very short hydrogen bond (2·437 Å) in $KH(HCOO)_2$ (Taurian, Lunell & Tellgren, 1987).

This work was supported by the Swedish Natural Science Research Council. One of us (NGF) is grateful to the Brazilian Post-Graduate Education Federal Agency (CAPES) for providing a Graduate Fellowship.

References

Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* **A30**, 129–147, 148–153.

Becker, P. J. & Coppens, P. (1975). *Acta Cryst.* **A31**, 417–425.

Chiari, G. & Ferraris, G. (1982). *Acta Cryst.* **B38**, 2331–2341.

Delaplane, R. G., Tellgren, R. & Olovsson, I. (1990). *Acta Cryst.* **B46**, 361–370.

Fernandes, N. G., Tellgren, R. & Olovsson, I. (1988). *Acta Cryst.* **C44**, 1168–1172.

Figgis, B. N., Reynolds, P. A. & Wright, S. (1983). *J. Am. Chem. Soc.* **105**, 434–440.

Fuess, H., Bats, J. W., Dannöhl, H., Meyer, H. & Schweig, A. (1982). *Acta Cryst.* **B38**, 736–743.

Fuess, H., Burger, N. & Bats, J. W. (1981). *Z. Kristallogr.* **156**, 219–232.

Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.

Hermansson, K. (1987). *Acta Chem. Scand. Ser. A*, **41**, 513–526.

Hirshfeld, F. L. (1971). *Acta Cryst.* **B27**, 769–781.

Hirshfeld, F. L. (1977). *Isr. J. Chem.* **16**, 226–229.

International Tables for Crystallography (1983). Vol. A, pp. 737–744. Dordrecht: Kluwer Academic Publishers.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* **A30**, 580–584.

Lundgren, J.-O. (1982). *Crystallographic Computer Programs.* Report UUIC-B13-04-05. Institute of Chemistry, Univ. of Uppsala, Sweden.

McIntyre, G. J., Ptasiewicz-Bak, H. & Olovsson, I. (1990). *Acta Cryst.* **B46**, 27–39.

NANTY, M. T. (1912). *Ann. Chim. Phys.* **27**, 7–29, 29–89.
NANTY, M. T. (1913). *Ann. Chim. Phys.* **28**, 77–131, 132–191, 191–208.
OHBA, S., TORIUMI, K., SATO, S. & SAITO, Y. (1978). *Acta Cryst.* B**34**, 3535–3542.
OLOVSSON, I. (1980). *Electron and Magnetization Densities in Molecules and Crystals*, edited by P. BECKER, pp. 831–894. New York: Plenum Press.
OLOVSSON, I. & JÖNSSON, P.-G. (1976). *The Hydrogen Bond – Recent Developments in Theory and Experiment*, Vol. 2, edited by P. SCHUSTER, G. ZUNDEL & C. SANDORFY, pp. 395–456. Amsterdam: North-Holland.
STEVENS, E. D., DELUCIA, M. L. & COPPENS, P. (1980). *Inorg. Chem.* **19**, 813–820.
TAURIAN, O. E., LUNELL, S. & TELLGREN, R. (1987). *J. Chem. Phys.* **86**, 5053–5059.

Acta Cryst. (1990). B**46**, 466–474

Structure and Electron Density of Pentasodium Trihydrogentetracarbonate

BY NELSON G. FERNANDES,* ROLAND TELLGREN AND IVAR OLOVSSON

Institute of Chemistry, University of Uppsala, Box 531, *S*-751 21 *Uppsala, Sweden*

(*Received* 13 *December* 1989; *accepted* 14 *February* 1990)

Abstract

$Na_5H_3(CO_3)_4$, $M_r = 358{\cdot}1$, triclinic, $P\bar{1}$, $a = 3{\cdot}4762\,(1)$, $b = 10{\cdot}0393\,(2)$, $c = 15{\cdot}5969\,(3)$ Å, $\alpha = 107{\cdot}770\,(2)$, $\beta = 95{\cdot}589\,(2)$, $\gamma = 95{\cdot}028\,(2)°$, $V = 511{\cdot}90\,(2)$ Å^3, $Z = 2$, $D_x = 2{\cdot}32$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71073$ Å, $\mu = 0{\cdot}379$ mm^{-1}, $F(000) = 356$, $T = 298$ K, $R(F^2) = 0{\cdot}0287$ for 8956 unique reflections. The carbonate groups are linked by hydrogen bonds to form two independent $[H_3(CO_3)_4]^{5-}$ fragments. There are four hydrogen bonds in the asymmetric unit, two of which are asymmetric with O···O distances of 2·572 (1) and 2·597 (1) Å. The other two are symmetric with O···O distances of 2·492 (1) and 2·507 (1) Å. Apparently, the H atoms in these symmetric hydrogen bonds are not located at inversion centres. Deformation densities in the covalent bonds of the carbonate groups are correlated with C—O bond order.

Introduction

The present study is part of a series of studies of short hydrogen bonds in hydrogen carbonates. Previous work has involved $KMgH(CO_3)_2.4H_2O$ and $KNiH(CO_3)_2.4H_2O$ (Fernandes, Tellgren & Olovsson, 1988, 1990).

The salt $Na_2CO_3.3NaHCO_3$ is reported to occur as the mineral wegscheiderite (Fahey & Yorks, 1963), a name given in honour of Wegscheider who was the first to synthesize it. Cell dimensions for the mineral and the synthetic crystal have been determined by Appleman (1963); optical properties have been measured by Fahey & Yorks (1963). Phase-equilibrium studies of the system Na_2CO_3–$NaHCO_3$–H_2O have been performed by Hill & Bacon (1927) and by Waldeck, Lynn & Hill (1934). Differential thermal analysis (Barral & Rogers, 1966) shows that it is an intermediary product of the decomposition of $NaHCO_3$. From Raman and IR spectral studies of undeuterated and deuterated powder samples at 298 and 93 K, Bertoluzza, Monti, Morelli & Battaglia (1981) predicted the main structure of the anion as discrete $[H_3(CO_3)_4]^{5-}$ units.

Experimental

The phase diagram of the ternary system $NaHCO_3$–Na_2CO_3–H_2O has been studied at several temperatures, from 298 to 323 K by Hill & Bacon (1927) and from 373 to 473 K by Waldeck, Lynn & Hill (1934). On this basis a composition was chosen such that the two phases in equilibrium at 373 K would be a saturated solution and the solid $Na_5H_3(CO_3)_4$. At room temperature Na_2CO_3 was completely dissolved in water and then $NaHCO_3$ was added. The system was sealed and kept in an electric oven at 373 K. After two weeks the solid material consisted of fibrous and needle-like crystals as was reported for the natural compound (Fahey & Yorks, 1963). A crystal with well developed faces of size 0·10 × 0·14 × 0·29 mm was selected and checked for twinning *etc.* by the Weissenberg technique. All subsequent X-ray measurements were performed on an automated Stoe–Philips four-circle diffractometer, graphite monochromator, λ(Mo $K\alpha$) = 0·71073 Å. Unit-cell parameters were determined from the refinement of 2θ angles of 104 reflections, $10 \leq 2\theta \leq 30°$; they agree qualitatively with the values reported for the mineral (Appleman, 1963). In this work the sequence of the unit-cell axes was chosen in agreement with the conventions for defining a reduced basis (*Inter-*

---

* Permanent address: Department of Chemistry, Federal University of Minas Gerais, CP 702, 30161 Belo Horizonte, Brazil.

0108-7681/90/040466-09$03.00