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Hydrogen Bond Studies.
CX.[*] A Neutron Diffraction and Deformation Electron Density Study of Sodium Hydrogen Oxalate Monohydrate, $NaHC_2O_4.H_2O$

BY ROLAND TELLGREN, JOHN O. THOMAS AND IVAR OLOVSSON

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

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The crystal structure of $NaHC_2O_4.H_2O$ has been studied with three-dimensional single-crystal neutron diffraction data. The hydrogen oxalate ions are linked end-to-end to form infinite chains by means of asymmetric hydrogen bonds [2·571 (1) Å] with an O–H distance of 1·036 (1) Å. The water molecules are involved in two hydrogen bonds; one is almost linear with an O–H···O angle of 171·8 (1)°, whereas the other is bent at 157·7 (1)°. Within the water molecules the O–H distances are 0·962 (2) and 0·963 (2) Å, and the H–O–H angle 107·8 (1)°. The deformation electron density within and around the hydrogen oxalate ion, the water molecule and the Na ion has been studied with the neutron-diffraction-determined positional and thermal parameters together with X-ray data collected out to sin θ/λ = 0·905 $Å^{-1}$.

Introduction

The crystal structures of normal and deuterated $NaHC_2O_4.H_2O$ have already been determined by X-ray diffraction methods (Tellgren & Olovsson, 1971). A neutron diffraction study has now been carried out, partly to give a more detailed description of the hydrogen-bond system, but primarily to form the basis for an $X - N$ deformation electron density study. Fresh X-ray data have also been collected for this purpose.

It has been suggested that it is only meaningful to perform density studies of this type at low temperature. It can be argued, however, that low-temperature studies have also shown that the theoretical advantages do not always outweigh the experimental difficulties which arise with cryostats and temperature matching. The first part of this investigation has thus been carried out at room temperature.

Unit cell and space group

The diffraction symmetry and lack of systematic absences in the neutron data confirmed the space group $P\bar{1}$ found in the previous X-ray work. Crystal data are summarized in Table 1.

Table 1. *Crystal data* (295 K)

Crystal system: triclinic
Space group: $P\bar{1}$

a = 6·5032 (8) Å
b = 6·6728 (7)
c = 5·6982 (8)
α = 85·036 (5)°
β = 109·997 (6)
γ = 105·016 (10)

V = 224·429 $Å^3$
Z = 2
D_x = 1·924 g cm^{-3}
μ_{obs} (neutrons) = 1·13 cm^{-1}
μ_{calc} (X-rays) = 5·77

Experimental

Neutron work

Sodium hydrogen oxalate monohydrate was prepared as described by Tellgren & Olovsson (1971). Large crystals were grown from an aqueous solution. The crystal used in the neutron diffraction work had six boundary planes [±(001); ±(11$\bar{1}$); ($\bar{1}$00) and (10$\bar{1}$)] and a volume of 38 mm^3.[†]

The data were collected at 295 K with a Hilger & Watts four-circle diffractometer controlled by a PDP-8 computer at the Swedish Atomic Energy R2 reactor at Studsvik. The neutron flux at the specimen was 1·3 × 10^6 n cm^{-2} s^{-1} at a wavelength of 1·210 Å. A region of reciprocal space out to sin θ/λ = 0·693 $Å^{-1}$ was examined with the $\omega/2\theta$ step-scan technique. [For further details of the experimental equipment see Tellgren (1975).]

Three standard reflexions were measured at regular intervals as a check on crystal and electronic stability. No significant changes were observed. 1243 independent reflexions were measured, of which 1066 had intensities greater than $3\sigma_{count}$. The intensities were corrected for Lorentz, absorption and secondary extinction effects (*cf. Refinement*). The linear absorption coefficient (μ) was determined experimentally to be 1·13 cm^{-1}, which corresponds to a value of 41·5 barns for the incoherent scattering cross-section for H.

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[*] Part CIX: Tellgren & Liminga (1977), *Ferroelectrics*, in the press.

[†] Details of the X-ray and neutron crystal morphology and orientation matrices have been deposited with the British Library Lending Division. See following footnote.

The resulting transmission factors were in the range 0·609–0·883.

X-ray work

The crystal used for the data collection was an elongated prism with six centrosymmetrically related faces ±(100), ±(010) and ±(001).

The data were collected at 295 K with a Stoe–Philips four-circle diffractometer operating in an $\omega/2\theta$ scan mode and controlled by a PDP-8/I computer.

Graphite-monochromated Mo radiation (λ = 0·71069 Å) was used to examine a region of reciprocal space out to $\sin\theta/\lambda = 0{\cdot}905$ Å^{-1}. 3523 reflexions were averaged to give 2779 unique reflexions with an agreement factor of 0·015. The raw intensities were corrected for Lorentz, polarization and absorption effects. The transmission factors were in the range 0·938–0·971 and the calculated absorption coefficient $\mu_c = 5{\cdot}77$ cm^{-1}.

Refinement

Neutron data

The structure was refined by minimizing the function $\Sigma\, w(|F_o| - |F_c|)^2$ with the full-matrix least-squares program *UPALS* (Lundgren, 1975). The reflexions were assigned weights inversely proportional to the estimated variance of the observations $w = 1/\sigma^2(F)$, where $\sigma^2(F) = \sigma^2_{\rm count}/4F^2 + (0{\cdot}020F)^2$. The first term is based on counting statistics and the second is an empirical correction term to take account of other errors in the data.

The refinement was based on the 1066 reflexions with intensities greater than $3\sigma_{\rm count}$. It comprised 33 positional, 66 anisotropic thermal parameters, 1 overall scale factor and 6 anisotropic extinction parameters. The final agreement factors were $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o| = 0{\cdot}021$, $R_w = [|\Sigma\, w(|F_o| - |F_c|)^2|/\Sigma\, w|F_o|^2|]^{1/2} = 0{\cdot}027$.

The standard deviation of an observation of unit weight was: $\sigma_1 = |\Sigma\, w(|F_o| - |F_c|)^2/(m-n)|^{1/2} = 1{\cdot}10$, where m is the number of observations and n is the number of parameters varied. The final parameters are given in Table 2.* In the last cycle of refinement the anisotropic (type 2) extinction parameters (W_{ij}) had the values 2·4 (2), 0·0 (1), 2·3 (2), −0·2 (1), 0·7 (2) and −0·9 (1) × 10^4 (Coppens & Hamilton, 1970).

Table 2. *Neutron and X-ray diffraction determined atomic coordinates* ($\times 10^5$)

The neutron values are given in the upper row.

	x	*y*	*z*
Na	25157 (17)	2760 (17)	24034 (19)
	25168 (6)	2759 (5)	24043 (6)
O(1)	24554 (12)	35585 (10)	34233 (12)
	24563 (11)	35541 (9)	34288 (12)
O(2)	26334 (12)	67188 (11)	17220 (12)
	26326 (13)	67243 (10)	17255 (11)
O(3)	33439 (10)	83228 (10)	61211 (11)
	33419 (10)	83252 (8)	61189 (11)
O(4)	23480 (12)	51494 (10)	76240 (12)
	23481 (12)	51441 (9)	76270 (11)
C(1)	25835 (8)	53910 (8)	35400 (9)
	25809 (12)	53874 (11)	35408 (13)
C(2)	27686 (8)	63939 (8)	59853 (9)
	27688 (12)	63948 (10)	59852 (12)
O(*W*)	14506 (12)	8182 (11)	81388 (13)
	14445 (13)	8147 (12)	81419 (13)
H(1)	18940 (25)	22316 (23)	76277 (29)
	18767 (330)	19783 (331)	76750 (335)
H(2)	20809 (28)	−163 (24)	74098 (28)
	20485 (304)	567 (202)	75326 (274)
H	25444 (23)	60393 (20)	1122 (23)
	25542 (278)	61245 (222)	2195 (327)

The coherent scattering amplitudes used were those tabulated by Bacon (1972).

As a final check on the tabulated values and also on the possibility of disorder in the structure, some cycles of refinement were carried out in which all scattering amplitudes except that of sodium were allowed to vary together with the 106 parameters referred to above. No parameter shifted significantly.

X-ray data

A few cycles of full-matrix least-squares refinement were made to assess the level of extinction in the crystal. Only one reflexion was found to have an extinction coefficient different from 1·00 [the 200 reflexion, $E_{\rm ext}(F) = 1{\cdot}01$]. The parameters are given in Table 2.* With the positional and thermal parameters fixed to their neutron values, the scale factor was refined and a Fourier file was written (*cf. Deformation electron densities*).

Reflexions with $|F_o| < 3\sigma_{\rm count}$ were not included either in the refinements or in the Fourier file.

The spherical X-ray form factors for non-hydrogen atoms were taken from Hanson, Herman, Lea & Skillman (1964) and for the H atoms from Stewart, Davidson & Simpson (1965). The scattering factors for non-hydrogen atoms were corrected for anomalous dispersion according to Cromer & Liberman (1970).

The calculations were all performed on the IBM 370/155 computer in Uppsala. The programs used are described by Lundgren (1975).

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* Lists of structure factors, neutron and X-ray thermal parameters, neutron r.m.s. displacements along the ellipsoid axes and details of the X-ray and neutron crystal morphology and orientation matrices have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32747 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* See previous footnote.

Description of the structure

General

The crystal structure of $NaHC_2O_4.H_2O$ as determined by neutron diffraction is not significantly different from that obtained earlier by X-ray diffraction (Tellgren & Olovsson, 1971). The general features of the structure are illustrated in Figs. 1 and 2. Bond distances and angles within the hydrogen oxalate ion, hydrogen-bond lengths and distances around the Na ion are given in Table 3. Comparison with the results of the X-ray studies reveals only minor differences in the non-hydrogen atom positions and the familiar shift in apparent H atom positions towards the atom to which the H is covalently bonded (Thomas, Tellgren & Almlöf, 1975). There are also no unexpected differences to be found in the anisotropic temperature factors from the different studies.

The hydrogen oxalate ions are linked end-to-end to form infinite chains by means of hydrogen bonds [2·571 (1) Å]. The chains are linked transversely to form layers both *via* O–H···O bonds from the water molecules and electrostatic Na^+···O forces. These layers are, in turn, held together by similar Na^+···O bonds. The hydrogen oxalate group is non-planar with an angle of twist between the COO planes about the C–C bond of 12·92 (4)°.

The hydrogen-bond system

The hydrogen-bond system is illustrated in Fig. 2, distances and angles are listed in Table 3. The hydrogen bond O(2)–H···O(4) which connects the hydrogen oxalate ions is asymmetric and approximately linear [O–H···O angle 176·2 (1)°]. The donor distance O(2)–H and the acceptor distance H···O(4) are 1·036 (1) and 1·537 (1) Å respectively.

The water molecule, with O–H distances 0·962 (2) and 0·963 (2) Å and an H–O–H angle of 107·8 (1)°, has a geometry very close to the average geometry for

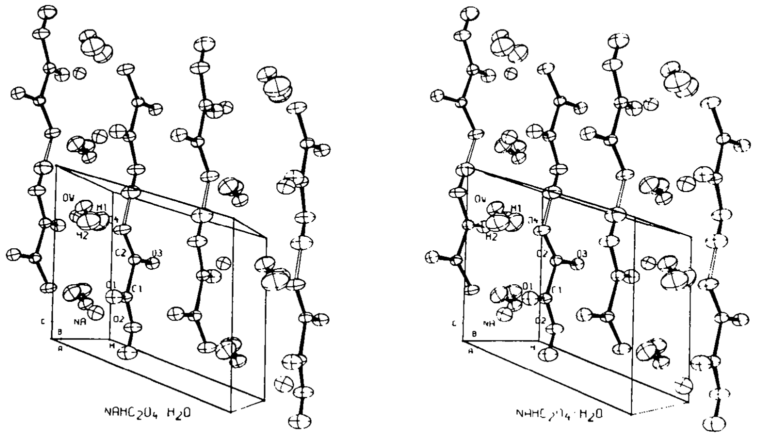

Fig. 1. A stereoscopic illustration showing part of the layers and the content of a unit cell. The ellipsoids are scaled to include 50% probability.

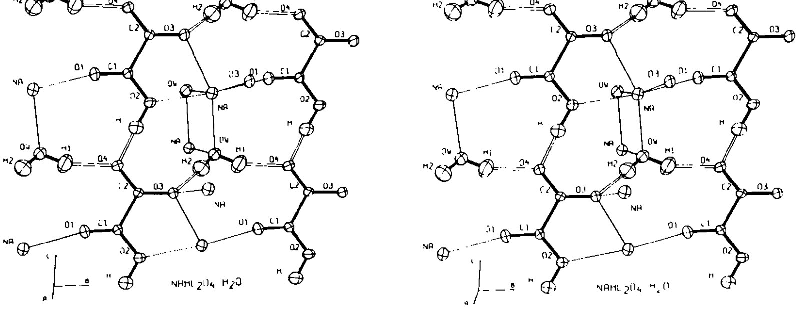

Fig. 2. A stereoscopic illustration showing the atomic arrangement and the hydrogen-bond system within a layer parallel to the *bc* plane. The immediate surroundings of some of the atoms are also shown.

Table 3. *Interatomic distances* (Å) *and angles* (°) *in* $NaHC_2O_4.H_2O$

Covalent bonds

$X-Y-Z$	$X-Y$	$Y-Z$	$\angle X-Y-Z$
O(1)–C(1)–O(2)	1·210 (1)	1·307 (1)	125·23 (6)
O(3)–C(2)–O(4)	1·245 (1)	1·249 (1)	127·25 (6)
C(1)–C(2)	1·552 (1)	Dihedral twist about the C–C bond 12·92 (4)	
H(1)–O(*W*)–H(2)	0·963 (2)	0·962 (2)	107·77 (14)

Ionic bonds

Na–O(*W*)	2·311 (1)
–O(1)	2·327 (1)
–O(3)	2·363 (1)
–O(*W*)′	2·408 (1)
–O(2)	2·462 (1)
–O(3)′	2·473 (1)

Hydrogen bonds

O–H···O	O–H	H···O	O···O
O(2)–H···O(4)	1·036 (1)	1·537 (1)	2·571 (1)
O(*W*)–H(1)···O(4)	0·963 (2)	1·892 (2)	2·806 (1)
O(*W*)–H(2)···O(3)	0·962 (2)	1·862 (2)	2·824 (1)

C–O–H···O–C	(∠C–O–H)	(∠O–H···O)	(∠H···O–C)
C(1)–O(2)–H···O(4)–C(2)	112·76 (9)	176·17 (13)	118·08 (7)
O(*W*)–H(1)···O(4)–C(2)		157·69 (14)	127·41 (7)
O(*W*)–H(2)···O(3)–C(2)		177·75 (14)	125·90 (7)

a water molecule in a crystalline hydrate: O–H distance 0·956 Å and H–O–H angle 107·8° (Ferraris & Franchini-Angela, 1972).

The water molecule acts as a donor in two fairly long hydrogen bonds, O(*W*)–H(1)···O(4) and O(*W*)–H(2)···O(3), with acceptor distances 1·892 (2) and 1·862 (2) Å respectively. It can also be noted from Fig. 2 that the environments of the two acceptor atoms, O(3) and O(4), are quite different. O(3) accepts only one hydrogen bond, the acceptor angle C(2)–O(3)···H(2) being 125·90 (7)° and the hydrogen-bond angle O(*W*)–H(2)···O(3) 177·8 (1)°. It does, however, lie very close to two Na ions. O(4), on the other hand, acts as acceptor in two hydrogen bonds with acceptor distances 1·537 (1) and 1·892 (2) Å. The acceptor angles are 118·1 (1) and 127·4 (1)°. The longer hydrogen bond O(*W*)–H(1)···O(4) is far from linear with a hydrogen-bond angle of 157·7 (1)°.

Deformation electron densities

The deformation electron density $\rho_{X-N}(\mathbf{r})$ at a point $\mathbf{r}$ in the unit cell is calculated by the expression

$$\rho_{X-N}(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{H}} (\mathbf{F}_{o,X} - k\mathbf{F}_{c,N}) \exp(-2\pi i\mathbf{H}.\mathbf{r})$$

(Coppens, 1974). The vector $\mathbf{F}_{o,X}$ is the observed X-ray structure amplitude with the appropriate phase. $\mathbf{F}_{c,N}$ is the calculated structure factor from the spherical free-atom X-ray scattering factors and the positional and thermal parameters obtained in the neutron diffraction study, and k is a calculated scale factor. For the present case of a centrosymmetric structure, the phase (sign) of $\mathbf{F}_{o,X}$ is assumed to be given by $\mathbf{F}_{c,N}$. The resulting maps are shown in Figs. 3–6. It has become the practice to quote the relative error in maps of this general quality as being ~0·05 e Å^{-3} at regions away from the atom centres. This figure has been arrived at on the basis of the appearance of chemically equivalent regions in the structures studied. We therefore quote 0·05 e Å^{-3} as a rough guide to the errors to be expected in the maps (away from atom centres).

The maps for the $HC_2O_4^-$ ion (Fig. 3) reveal some interesting features. (*Note*: the two ends are plotted separately because of the 12·9° twist in the ion about the C–C bond.) There is a markedly higher density in the O(1)–C(1)–C(2)–O(3) bonds (0·40 e Å^{-3}) than in

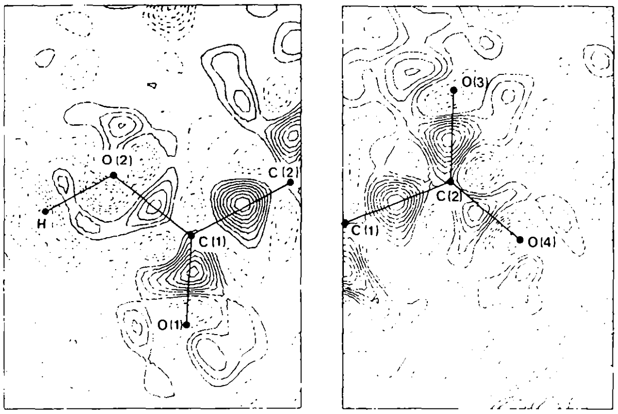

Fig. 3. $X-N$ difference electron density maps for the two ends of the $HC_2O_4^-$ ion. Here and elsewhere contours are drawn at intervals of 0·05 e Å^{-3}. The zero-level contour has been omitted.

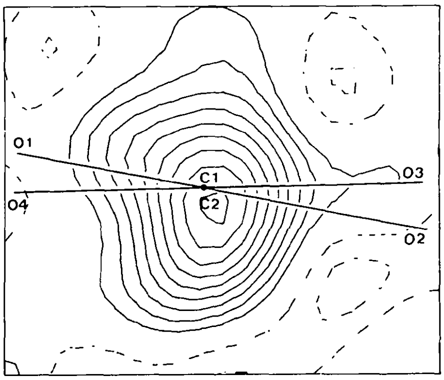

Fig. 4. $X-N$ difference electron density halfway between C(1) and C(2) in a plane perpendicular to the C(1)–C(2) direction.

C(1)–O(2) and C(2)–O(4) (0·20 and 0·25 e Å^{-3} respectively). This can be interpreted as being evidence of a partially conjugated π system involving atoms O(1), C(1), C(2) and O(3): a system in which O(2) and O(4) are less able to participate by virtue of their involvement in the strong hydrogen bond O(2)–H···O(4). The existence of such a π-system would also account for the planarity of $HC_2O_4^-$ ions found in different structure determinations (*cf.* Table 3, Thomas & Renne, 1975). A section perpendicular to the C–C bond taken at the bond centre is shown in Fig. 4.

It would have seemed reasonable to interpret the difference in deformation density in the C(1)–O(1) and C(1)–O(2) bonds [lengths 1·210 (1) and 1·307 (1) Å respectively] as reflecting the difference in bond strengths. However, the situation for C(2)–O(3) and C(2)–O(4) [lengths 1·245 (1) and 1·249 (1) Å respectively] raises serious doubts as to the validity of using peak height alone as an indication of bond strength. The lower peak density in C(2)–O(4) is presumably related to the role of O(4) as hydrogen-bond acceptor. The difference density in the O(2)–H···O(4) hydrogen bond has a familiar appearance: covalent (though weak) bonding density in O(2)–H, together with a region of electron deficiency between H and the lone-pair lobe at the acceptor site on O(4).

The water molecule (Fig. 5) shows two O–H bonds with essentially equivalent bond-density peaks of 0·15 e Å^{-3}. [H···O distances: 1·862 (2) and 1·892 (2) Å]. For the water molecule in $LiHCOO.H_2O$ (Thomas, Tellgren & Almlöf, 1975) peak bond densities of ~0·00 and ~0·15 e Å^{-3} have been found for H···O distances of 1·742 (3) and 1·949 (4) Å respectively. The evidence available at present is insufficient to suggest any general trends. The electron distribution within the water molecules of crystal hydrates is, however, the subject of a current project at this Institute.

Fig. 6 shows the region between the Na ion and the water O atom. The electron density around the Na ion is clearly non-spherical, with the most positive side of the Na ion directed towards the lone-pair region of the water O atoms. A similar electron distribution has been obtained around the Cr atom in $C_6H_6Cr(CO)_3$ (Rees & Coppens, 1973). It should be remembered, however, that the largest errors in $X-N$ maps arise in the vicinity of the nuclei.

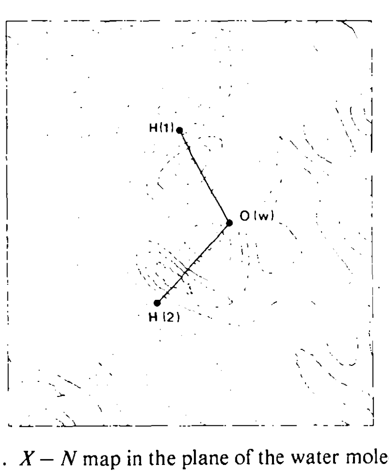

Fig. 5. $X-N$ map in the plane of the water molecule.

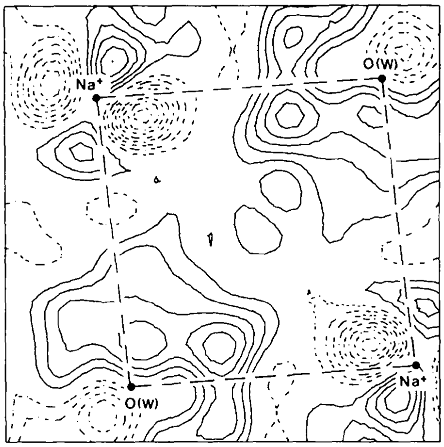

Fig. 6. $X-N$ map in a plane through two water O atoms and two Na ions.

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