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Structure of the Adipate Complex $[Na_2(C_6H_9O_4)_2(C_6H_{10}O_4)].2H_2O$ from Neutron Diffraction at 220 and 295 K

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Abstract

The crystal structure of sodium hydrogen adipate–adipic acid (2/1) dihydrate, $[Na_2(C_6H_9O_4)_2(C_6H_{10}O_4)].2H_2O$, $M_r = 518{\cdot}4$, has been determined from neutron diffraction data collected at 220 and 295 K. Crystals are monoclinic, space group $C2/m$, with $Z = 2$. At 295 K, $a = 9{\cdot}378\,(2)$, $b = 13{\cdot}379\,(5)$, $c = 10{\cdot}247\,(3)$ Å, $\beta = 95{\cdot}93\,(3)°$, $V = 1278{\cdot}8\,(7)$ Å^3, $D_n = 1{\cdot}346$, $D_m = 1{\cdot}348\,(1)$ g cm^{-3} (in dibromomethane/bromobutane), $\lambda = 1{\cdot}1588\,(2)$ Å, $\mu = 2{\cdot}186$ cm^{-1}, $F(000) = 176{\cdot}4$ fm, $R(F^2) = 0{\cdot}108$ for all 1995 non-equivalent reflections with $\sin\theta/\lambda < 0{\cdot}71$ Å^{-1}. The crystal structure is similar at 220 K except for reduced nuclear mean-square displacements. Hydrogen adipate subunits (called *A*) are linked end-to-end in infinite chains by very short O···O (2·44 Å) hydrogen bonds where the H nuclei are on centers of symmetry within the experimental error. The Na cation is octahedrally coordinated by O atoms from molecules *A* and also by non-ionized adipic acid molecules (called *B*). The *B* molecules have large mean-square nuclear displacements which are described in terms of anharmonicity and disorder.

Introduction

The present study was undertaken in order to determine the charge density distribution in the crystal structure of a salt of a simple carboxylic acid. An earlier candidate for such a study was lithium hydrogen adipate (He & Craven, 1984), but the crystals were unsuitable because the X-ray intensities were considered to be affected by excessive extinction. We turned to the sodium salt, but the crystals were again unsuitable for a charge density study because, as described below, some of the atoms in the structure have large mean-square displacements and are disordered. Nevertheless, the structure has some unusual features which we have investigated using neutron diffraction.

Although it would appear to be straightforward to obtain crystals of sodium adipate or sodium hydrogen adipate from aqueous solution by addition of sodium hydroxide or sodium carbonate to adipic acid, our repeated efforts to do so were unsuccessful. The product was instead a crystalline hydrated complex of adipic acid with sodium hydrogen adipate. The crystal structure (Fig. 1) was first determined from X-ray diffraction (Gao, Clancy & Craven, 1986), but the chemical nature of the structure remained uncertain because it depended critically

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upon establishing the location of the H atoms. The various dicarboxylic acid species present might be doubly ionized, singly ionized, the free acid, or the intermediate in which H atoms are equally shared in the bridging of neighboring adipates. There were also difficulties because the space group (*C*2, *Cm* or *C*2/*m*) is not determined uniquely from systematic absences in the X-ray diffracted intensities. While the space group *C*2/*m* seemed to be suitable for describing most of the crystal structure, our X-ray study indicated that one of the two distinct adipate species in the crystal might be either disordered in this space group or ordered in one of the lower symmetry space groups. For these reasons, we have carried our redeterminations of the crystal structure from two sets of neutron diffraction data collected at 295 and 220 K.

Experimental

Crystals of the complex were first obtained by reaction of equimolar amounts of adipic acid with sodium carbonate (Na_2CO_3) in water. These crystals were also obtained by slow evaporation at room temperature of aqueous solutions containing adipic acid and sodium hydroxide in the mole ratios 1:1·2 through to 1:1·6, but not if the composition was outside this range. Deuterated starting materials were used in efforts to obtain crystals with the non-methylene H atoms exchanged, but the resulting thin plates were too small for neutron diffraction data collection. There were no such difficulties with the hydrogenated crystals. Therefore, they were used both for our X-ray and neutron studies.

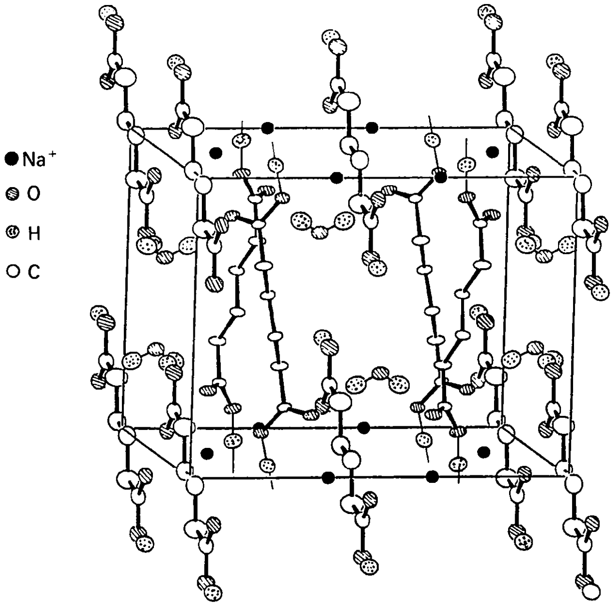

Fig. 1. The crystal structure with atoms represented by 50% probability ellipsoids (Johnson, 1976). Methylene H atoms are omitted for clarity. The *b* axis is horizontal, while *c* is vertical.

Large single crystals (~6 mg) were used for differential scanning calorimetry in the temperature range from 120 to 400 K, using a Mettler TA4000 system. Upon heating, irreversible decomposition was observed at 352 K with $\Delta H_{\text{endo}} = 23{\cdot}3$ kJ mol^{-1} of water present in the crystal. When observed near this temperature on a heated microscope stage, a single crystal developed small beads on its surface. We conclude that crystal decomposition is associated with the loss of water of crystallization. Upon cooling from room temperature, no crystal phase transition was observed down to 120 K which was our target for reduced-temperature neutron data collection.

The crystals are monoclinic and appear to belong to the class 2/*m*. They are plates with prominent (001) faces, exhibiting also the forms {100}, {010} and {110}, and they are readily cleaved on (010). The crystal structure was first determined from 1915 non-symmetry-related X-ray reflections with $\sin\theta/\lambda < 0{\cdot}70$ Å^{-1} collected at room temperature with Nb-filtered Mo $K\alpha$ radiation (Gao, Clancy & Craven, 1986). The structure was refined by full-matrix least squares to give $wR = 0{\cdot}07$, assuming the crystal composition to be $Na_2(C_6H_9O_4)_2(C_6H_{10}O_4).2H_2O$, with two formula units per unit cell in the space group *C*2/*m*. For reasons given above, we questioned that this was the correct composition. However, the subsequent neutron study has confirmed the X-ray results. Further details of the X-ray study will not be presented here because the neutron diffraction data gave more accurate nuclear positional and mean-square-displacement parameters, particularly for the H atoms.

Neutron data were collected at the Brookhaven High Flux Beam Reactor using a monochromated beam from the (220) planes of a Ge single crystal in transmission geometry having a wavelength of 1·1588 (2) Å as determined by diffraction from a standard KBr crystal ($a_o = 6{\cdot}6000$ Å at 295 K). The low-temperature procedures of measurement followed those earlier decribed by Weber, Craven & McMullan (1983). The sample crystals were maintained within 0·5 K of preset values with a closed-cycle helium refrigerator.† Measurements were made first at 295 K to complement the X-ray data and then at reduced temperatures. A crystal sample weighing 4·8 mg was mounted with $-a^*$ approximately 4° from the φ axis of the four-circle diffractometer. This crystal was used for measurements of

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† Air Products and Chemicals, Inc., Displex Model CS-202. The reported temperatures include a correction of +2·0 K based on a prior calibration with reference to the magnetic phase transition at $T_N = 78{\cdot}38\,(1)$ K in FeF_2 (Hutchings, Schulhof & Guggenheim, 1972).

Table 1. *Unit-cell dimensions*

Temp. (K)	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	*V* (Å^3)
220	9·349 (3)	13·286 (7)	10·260 (6)	95·29 (3)	1269·0 (11)
295	9·378 (2)	13·379 (5)	10·247 (3)	95·93 (2)	1278·8 (7)
295*	9·372 (3)	13·368 (4)	10·242 (3)	96·01 (3)	1276·1 (7)

*X-ray data from Gao, Clancy & Craven (1986).

the lattice parameters and the intensity data at 295 K but was fractured when cooled below 220 K. Since additional delay caused by loss of the crystal could not be afforded if the low-temperature measurements were to be completed during the available reactor period, it was decided to collect data at 220 K rather than 123 K, the original target temperature. For these measurements, a second crystal weighing 12·0 mg was mounted with [110] approximately along the φ axis. The unit-cell parameters (Table 1) were determined by a least-squares fit to $\sin^2\theta$ values of 40 reflections with $36 < 2\theta < 67°$ at 295 K and 32 reflections with $55 < 2\theta < 68°$ at 220 K. At both temperatures, intensity data were collected for one quadrant of reciprocal space using $\omega/2\theta$ step scans with a constant scan width of 3° for reflections up to $\sin\theta/\lambda = 0{\cdot}41$ Å^{-1}. Beyond this value up to the maximum $\sin\theta/\lambda = 0{\cdot}71$ Å^{-1}, scan widths were given by $\Delta 2\theta = (3{\cdot}460 + 1{\cdot}955\tan\theta)°$ at 295 K, and by $\Delta 2\theta = (2{\cdot}37 + 2{\cdot}77\tan\theta)°$ at 220 K. Indices were in the range *h* 0 to 13, *k* 0 to 18 and *l* −14 to 14. Intensities of two reflections, monitored after every 50 reflections, were constant within 2%. Integrated intensities were evaluated assuming that the background consisted of the first and last tenths of the total number of scan steps. The data were corrected for neutron absorption effects by an analytical procedure (de Meulenaer & Tompa, 1965; Templeton & Templeton, 1973) with $\mu = 2{\cdot}186$ cm^{-1} calculated taking the mass absorption coefficient for bonded hydrogen to be 26·4 m^2 kg^{-1} at $\lambda = 1{\cdot}1588$ Å (McMullan & Koetzle, 1979). The absorption corrections to the integrated intensities ranged from 1·588 to 1·125. After averaging multiple observations there were 1995 reflections, including 310 with $F^2 < 0$ and 812 with $F^2 > 3\sigma$ at 295 K. At 220 K, there were a total of 1927 reflections, 174 with $F^2 < 0$ and 1080 with $F^2 > 3\sigma$. Values of $R_{\rm int}(F^2)$ were 0·040.

Starting with the atomic parameters obtained from the X-ray study, 163 variables consisting of the scale factor, isotropic extinction parameter, nuclear positional and anisotropic thermal parameters were refined by full-matrix least squares using program *NOOT* (Craven & Weber, 1987). With all reflections included, the residual $\sum w(F_o^2 - F_c^2)^2$ was minimized where $w = \sigma^{-2}(F^2)$ and $\sigma^2(F^2) = \sigma^2_{\rm counts} + (0{\cdot}02F^2)^2$. Coherent scattering lengths for C, O, H and Na were taken from Koester (1977). The refinement converged with $R(F^2) = 0{\cdot}090$ and 0·125, $wR(F^2) = 0{\cdot}104$ and 0·111 and $S = 1{\cdot}658$ and 1·459 at 220 and 295 K respectively.* Neutron extinction was not severe [g = 0·09 (1) and 0·27 (2) × 10^{-4} rad]. The reflection most affected, assuming a type-I crystal with Lorentzian mosaicity (Becker & Coppens, 1974) was 001 with a correction $0{\cdot}82F_c^2$. Further details of these initial refinements have been given by Gao (1988).

Fourier syntheses of neutron scattering density confirmed the approximate H-atom positions determined in the X-ray study. Peaks in the scattering density for the methylene H atoms were found to be very diffuse for those of the adipic acid molecule (*B*) when compared with those of the hydrogen adipate species (*A*). As can be seen in Fig. 2, the mean-square-displacement ellipsoids for molecule *B* are larger than those of molecule *A*. Elongation of the ellipsoids in the direction of the long molecular axis was also observed for the heavier atoms in our X-ray study. Difference Fourier syntheses of neutron scattering density (Fig. 3) showed large residual features, up to 8% of the maximum in the map of

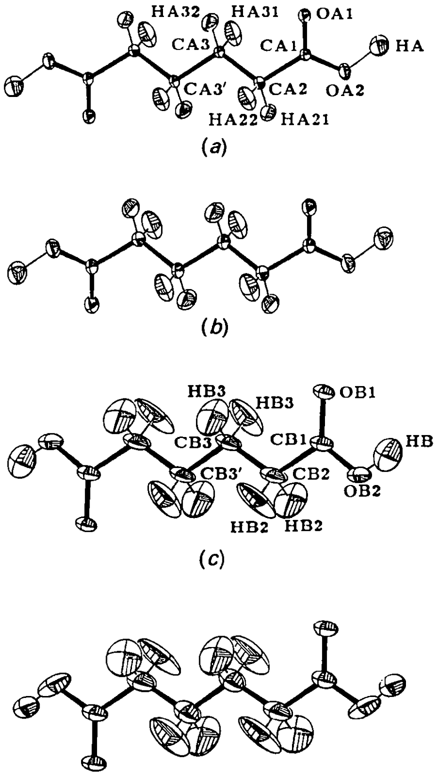

Fig. 2. Atomic nomenclature and thermal ellipsoids at 50% level of probability (Johnson, 1976). From top to bottom, the four molecules are: (*a*) hydrogen adipate at 220 K, (*b*) hydrogen adipate at 295 K, (*c*) adipic acid at 220 K, (*d*) adipic acid at 295 K.

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* $R(F^2) = (\sum|\Delta|)/\sum F_o^2)$, $wR(F^2) = [(\sum w\Delta^2)/(\sum wF_o^2)^2]^{1/2}$, $S = [(\sum w\Delta^2)/(m-n)]^{1/2}$, where $\Delta = (F_o^2 - F_c^2)$.

the scattering density itself. These were all associated with atoms of the adipic acid molecule *B*, indicating that the assumed structure model for this molecule was inadequate. If the space group is *C*2/*m*, then molecule *B* lies in the special position (*a*) with point symmetry 2/*m* so that the crystallographic twofold axis passes through the midpoint of the C*B*3—C*B*3′ bond. In the space group *C*2/*m*, efforts were made to fit the observed scattering density with molecule *B* having fixed standard values for bond lengths and angles and assuming disorder over two almost superposed sites. Some models tested involved displacement of the C atoms from the mirror plane $y = \frac{1}{2}$ and others involved translation of the molecule in the direction of the long molecular axis. We also considered ordered structures in the lower symmetry space group *C*2 in which atoms of the adipic acid molecule *B* were displaced from the plane $y = \frac{1}{2}$ and other ordered structures in space group *Cm* in which molecule *B* was translated within the mirror plane along the direction of the long molecular axis. However, none of these models gave improved agreement in the structure factors and none would refine satisfactorily by least squares. At this stage, we accepted the suggestion by Marsh (1986) that, unless a clear choice can be made in favor of a noncentrosymmetric model, it is better to describe a structure as centrosymmetric, even though disorder may need to be invoked.

It was decided that the large nuclear mean-square displacements for molecule *B* might be satisfactorily treated in space group *C*2/*c* if the atomic displacement factors were expanded to include anharmonic terms. This was done by introducing third- and fourth-order parameters according to the Gram–Charlier expression as defined in Table 2 and given by Johnson & Levy (1974) as their equation 5.2.3(9). In refinements with both the 295 and 220 K data, these higher order parameters were included as variables for all atoms. However, in neither case were the values obtained significantly different from zero for the atoms of the hydrogen adipate species, the water molecule and the sodium ion. Least-squares refinement was completed with the 107 additional variables used to describe the anharmonic vibration for molecule *B*. In addition to those higher order displacement parameters constrained to be zero by crystal symmetry, others were set to zero if they were found to be smaller than $1{\cdot}0\sigma$, or if they were strongly correlated with nuclear positional or

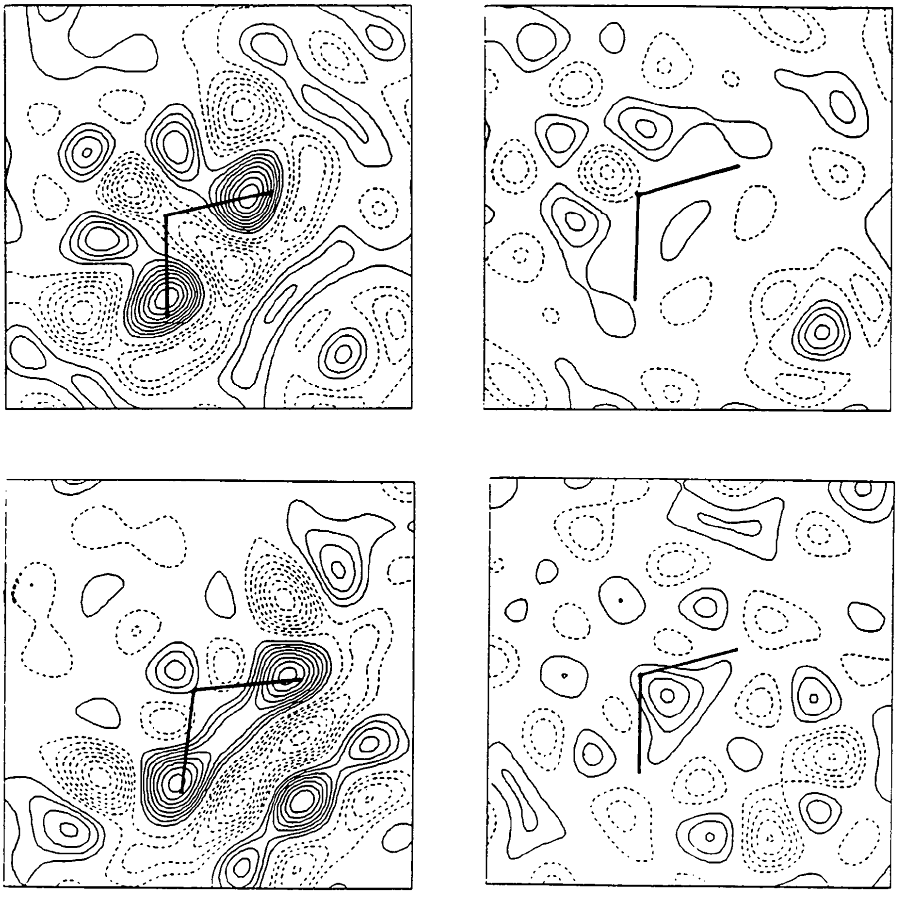

Fig. 3. Sections in the difference Fourier syntheses of neutron scattering density at 220 K in the plane of the adipic acid methylene groups containing C*B*2 (above) and C*B*3 (below). Maps on the left were obtained after refinement with the harmonic model for thermal vibrations, and on the right after refinement with the anharmonic model. Dashed contours are for negative density, solid are positive.

Table 2. *Nuclear positional and thermal parameters*

For each atom, entries are from the refinement with 220 K data and anharmonic temperature factors. The expression for the temperature factor is: $T = T_2(1 + T_3 + T_4)$ where T_2, T_3 and T_4 are given below. Entries without e.s.d.'s (given in brackets) are constrained by crystal symmetry. Parameters denoted by — were constrained to zero in the final refinement cycle if they were insignificantly different from zero ($< 1\sigma$) in earlier cycles, or if they were involved in correlations having coefficients > 0·90.

(*a*) Atomic positional and anisotropic thermal parameters

Anisotropic displacement parameters (Å^2) are given by the expression $T_2 = \exp[-2\pi^2\sum_i\sum_j h_i h_j a_i^* a_j^* U_{ij}]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na	0	0·3653 (2)	0	0·024 (1)	0·034 (2)	0·024 (1)	0	0·001 (1)	0
O*W*	0·4508 (4)	0	0·3377 (3)	0·063 (2)	0·054 (2)	0·035 (1)	0	0·005 (1)	0
O*A*1	0·3595 (2)	0·1605 (1)	0·1843 (1)	0·033 (1)	0·057 (1)	0·022 (1)	0·013 (1)	0·004 (1)	0·001 (1)
O*A*2	0·1866 (2)	0·2594 (1)	0·0982 (1)	0·044 (1)	0·053 (1)	0·024 (1)	0·019 (1)	0·010 (1)	0·008 (1)
C*A*1	0·2494 (1)	0·2101 (1)	0·1943 (1)	0·025 (1)	0·037 (1)	0·017 (1)	0·002 (1)	0·003 (1)	− 0·002 (1)
C*A*2	0·1810 (1)	0·2155 (1)	0·3218 (1)	0·025 (1)	0·066 (1)	0·019 (1)	− 0·001 (1)	0·003 (1)	− 0·002 (1)
C*A*3	0·2859 (1)	0·2451 (1)	0·4369 (1)	0·024 (1)	0·050 (1)	0·018 (1)	0·002 (1)	0·004	− 0·002 (1)
O*B*1	0·1405 (3)	0·5	0·0971 (2)	0·030 (3)	0·043 (3)	0·051 (3)	0	− 0·013 (2)	0
O*B*2	0·2253 (9)	0·5	0·3059 (10)	0·049 (4)	0·080 (7)	0·047 (6)	0	− 0·015 (6)	0
C*B*1	0·2409 (2)	0·5	0·1829 (5)	0·037 (4)	0·042 (3)	0·058 (4)	0	− 0·019 (3)	0
C*B*2	0·3955 (4)	0·5	0·1524 (3)	0·031 (4)	0·125 (6)	0·075 (6)	0	− 0·019 (3)	0
C*B*3	0·4239 (3)	0·5	0·0126 (3)	0·028 (3)	0·095 (3)	0·074 (6)	0	− 0·017 (4)	0
H*A*	0·25	0·25	0	0·067 (6)	0·069 (7)	0·061 (2)	0·033 (6)	0·007 (6)	0·012 (6)
H*A*21	0·1374 (4)	0·1416 (3)	0·3399 (3)	0·093 (3)	0·109 (3)	0·043 (2)	− 0·057 (3)	0·019 (2)	− 0·013 (2)
H*A*22	0·0912 (3)	0·2672 (3)	0·3100 (2)	0·043 (1)	0·147 (4)	0·036 (1)	0·039 (2)	0·004 (1)	− 0·005 (2)
H*A*31	0·3717 (3)	0·1904 (3)	0·4495 (2)	0·047 (2)	0·111 (3)	0·038 (1)	0·035 (2)	− 0·001 (1)	− 0·010 (2)
H*A*32	0·3357 (4)	0·3164 (3)	0·4155 (3)	0·088 (2)	0·081 (2)	0·040 (1)	− 0·036 (2)	0·015 (2)	− 0·003 (2)
H*W*	0·4142 (4)	0·0566 (3)	0·2918 (4)	0·074 (2)	0·079 (3)	0·068 (2)	0·003 (2)	0·011 (2)	− 0·007 (2)
H*B*2	0·4434 (8)	0·4389 (11)	0·1962 (10)	0·080 (5)	0·256 (18)	0·178 (9)	0·094 (7)	0·023 (5)	0·138 (9)
H*B*3	0·3758 (8)	0·4404 (9)	− 0·0290 (9)	0·098 (4)	0·209 (10)	0·159 (7)	− 0·089 (5)	0·040 (4)	− 0·099 (7)
H*B*	0·1308 (27)	0·5	0·3224 (22)	0·134 (10)	0·081 (11)	0·094 (12)	0	0·024 (12)	0

(*b*) Third-order thermal parameters (× 10^7)

The parameters are given by expression $T_3 = -\frac{4}{3}\pi^3 i\sum_j\sum_k\sum_l h_j h_k h_l c_{jkl}$.

jkl	O*B*2	C*B*1	H*B*2	H*B*3	H*B*
111	59 (21)	—	41 (33)	171 (39)	969 (270)
222	0	0	157 (92)	260 (40)	0
333	—	37 (15)	− 278 (70)	210 (57)	58 (55)
112	0	0	− 8 (34)	− 77 (24)	0
122	—	—	54 (55)	—	54 (28)
113	− 44 (16)	—	− 135 (26)	195 (29)	272 (108)
133	—	—	− 211 (33)	233 (34)	171 (66)
223	—	—	− 106 (58)	—	33 (15)
233	0	0	− 263 (50)	− 198 (35)	0
123	0	0	− 165 (34)	− 154 (24)	0

(*c*) Fourth-order thermal parameters (× 10^8)

The parameters are given by the expression $T_4 = \frac{2}{3}\pi^4\sum_i\sum_j\sum_k\sum_l h_i h_j h_k h_l d_{ijkl}$.

ijkl	O*B*1	O*B*2	C*B*1	C*B*2	C*B*3	H*B*2	H*B*3	H*B*
1111	− 7 (11)	− 13 (18)	2 (14)	− 16 (14)	− 5 (11)	− 69 (30)	− 285 (35)	− 181 (77)
2222	5 (4)	4 (5)	—	− 71 (10)	40 (15)	− 475 (41)	− 318 (29)	7 (15)
3333	—	4 (3)	7 (13)	− 4 (17)	− 30 (13)	− 97 (68)	− 116 (49)	140 (57)
1112	0	0	0	0	0	− 85 (23)	301 (26)	0
1222	0	0	0	0	0	− 261 (32)	274 (29)	0
1113	3 (6)	8 (11)	− 1 (7)	—	− 12 (9)	− 64 (21)	− 197 (27)	247 (66)
1333	8 (5)	14 (8)	13 (7)	14 (8)	19 (8)	− 146 (33)	− 189 (33)	100 (53)
2223	0	0	0	0	0	− 388 (42)	349 (34)	0
2333	0	0	0	0	0	− 283 (40)	261 (32)	0
1122	3 (2)	2 (5)	—	− 16 (12)	− 3 (5)	− 152 (26)	− 288 (27)	34 (22)
1133	− 3 (4)	− 9 (8)	0 (6)	− 8 (6)	− 5 (5)	− 102 (23)	− 193 (27)	100 (60)
2233	2 (2)	− 12 (15)	2 (2)	16 (8)	14 (7)	− 371 (43)	− 323 (32)	7 (9)
1123	0	0	0	0	0	− 140 (20)	225 (21)	0
1223	2 (3)	2 (7)	− 2 (2)	12 (5)	2 (4)	− 236 (26)	− 272 (25)	27 (11)
1233	0	0	0	0	0	− 193 (25)	229 (23)	0

the second-order U_{ij} parameters (correlation coefficients exceeding 0·90). Convergence was obtained with $R(F^2) = 0{\cdot}068$ and 0·108, $wR(F^2) = 0{\cdot}074$ and 0·090 and $S = 1{\cdot}223$ and 1·212 for the structure at 220 and 295 K respectively. The most significant differences from the previous refinement with harmonic parameters were 4·3σ for y(H*B*) and an increase of 8·9σ in U_{22} for H*B*2. As can be seen in Fig. 3, the final difference Fourier after the refinement with anharmonic parameters shows a considerable reduction in the residual scattering density around molecule *B*. The nuclear parameters from these refinements are in Table 2.* Correspond-

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* Nuclear positional and thermal parameters from the anharmonic 295 K refinement, together with lists of reflection data for the anharmonic refinement at both temperatures, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53798 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

ing interatomic distances, bond angles and torsion angles are in Table 3.

Discussion

Molecular geometry and crystal packing

The hydrogen adipate species (*A*) occupies a special position on a crystallographic center of symmetry. It has typical C—C bond lengths and C—C—C angles (Table 3). Average C—C bond lengths are 1·515 (5) Å at 220 K and 1·512 (6) Å at 295 K in good agreement with corresponding values from X-ray diffraction studies of lithium hydrogen adipate (1·516 Å; He & Craven, 1984) and piperazinium adipate (1·506 Å; Vanier & Brisse, 1983). The average C—H bond length at 220 K is a little shorter (1·085 Å) than has been obtained for methylene groups in other neutron diffraction studies, such as γ-aminobutyric acid (1·096 Å; Weber, Craven & McMullan, 1983). The effect may be due to the absence of thermal vibration corrections for the C—H distances, although such corrections are usually small (Craven & Swaminathan, 1984). The carboxylate groups are twisted out of the plane of the hydrocarbon backbone with a torsion angle about the C*A*1—C*A*2 bond of 53·7 (1)° at 220 K and 51·9 (2)° at 295 K. The conformation is similar to that observed in the crystal structures of adipic acid (Housty & Hospital, 1965) and for the dianion in piperazinium adipate (Vanier & Brisse, 1983). The hydrogen adipate subunits, each carrying a formal negative charge, are linked end-to-end in chains along the *c*-axis direction (Fig. 4) by means of short symmetric hydrogen bonds O*A*2···H*A*···O*A*2′ with O···O distance 2·443 (2) Å at 220 K and 2·449 (3) Å at 295 K. The H*A* nucleus lies on a crystallographic center of symmetry. In one refinement, fourth-order displacement parameters were introduced for the H*A* nucleus in order to allow for a possible bimodal probability density function (p.d.f.) or disorder. Values for all these parameters were insignificantly different from zero, indicating that the p.d.f. for H*A* can be described within experimental error in terms of the usual Gaussian p.d.f. The mean-square displacement for the central H*A* is 0·060 (6) Å^2 along the O···O direction.

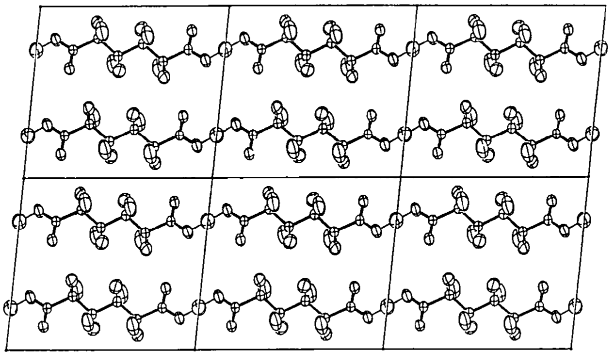

Fig. 4. Projection down the *b* axis, showing the arrangement of hydrogen adipate chains parallel to *c* (Johnson, 1976).

Table 3. *Internuclear distances* (Å), *angles* (°) *and torsion angles* (°) *from anharmonic refinement*

Values for 220 K (above) and 295 K (below) are uncorrected for the effects of thermal vibration.

(*a*) Internuclear distances

CA1—OA1	1·235 (2)	CB1—OB1	1·226 (5)
	1·232 (3)		1·224 (7)
CA1—OA2	1·280 (2)	CB1—OB2	1·284 (10)
	1·276 (2)		1·315 (10)
CA1—CA2	1·509 (2)	CB1—CB2	1·507 (5)
	1·512 (3)		1·499 (11)
CA2—CA3	1·516 (2)	CB2—CB3	1·483 (5)
	1·506 (3)		1·483 (11)
CA3—CA3′	1·519 (1)	CB3—CB3′	1·469 (4)
	1·519 (3)		1·472 (8)
OA2—HA	1·222 (2)	OB2—HB	0·914 (26)
	1·224 (2)		0·944 (39)
CA2—HA21	1·086 (4)	CB3—HB3	0·988 (10)
	1·067 (6)		0·994 (23)
CA2—HA22	1·083 (4)	CB2—HB2	1·012 (12)
	1·080 (5)		1·023 (20)
CA3—HA31	1·081 (3)	OW—HW	0·936 (5)
	1·076 (5)		0·923 (8)
CA3—HA32	1·087 (4)	OW···OA1^{i,vi}	2·739 (3)
	1·078 (5)		2·751 (6)
Na···OA^{ii,v}	2·424 (4)	OA1···HW	1·811 (4)
	2·438 (5)		1·835 (6)
Na···OA2^{i,iii}	2·390 (4)	OW···OB2^{vii}	2·617 (10)
	2·396 (5)		2·543 (24)
Na···OB^{i,iv}	2·383 (4)	OW···HB^{vii}	1·705 (25)
	2·409 (5)		1·600 (32)

(*b*) Bond angles

OA1—CA1—OA2	122·4 (1)	OB1—CB1—OB2	123·8 (5)
	122·5 (2)		120·0 (11)
OA2—CA1—CA2	116·3 (1)	OB2—CB1—CB2	113·7 (5)
	116·3 (2)		117·7 (1)
OA1—CA1—CA2	121·3 (1)	OB1—CB1—CB2	122·5 (3)
	121·3 (2)		122·3 (6)
CA1—CA2—CA3	113·1 (1)	CB1—CB2—CB3	117·5 (3)
	113·1 (2)		118·3 (7)
CA2—CA3—CA3′	112·4 (1)	CB2—CB3—CB3′	115·6 (3)
	112·7 (2)		116·8 (6)
CA1—OA1—HA	111·1 (1)	CB1—OB1—HB	112·4 (18)
	111·4 (2)		114·0 (28)
HA21—CA2—HA22	107·1 (3)	HB2—CB2—HB2^{v}	106·7 (9)
	106·9 (4)		110·7 (16)
HA21—CA2—CA1	107·5 (2)	HB3—CB3—HB3^{v}	106·6 (9)
	107·4 (3)		106·1 (19)
HA21—CA2—CA3	109·1 (2)	OW—HW···OA1	171·6 (4)
	109·4 (3)		170·9 (7)
HA22—CA2—CA1	108·6 (2)	HW—OW—HW^{v}	107·1 (5)
	108·9 (3)		107·5 (8)
HA22—CA2—CA3	111·2 (2)	OB2—HB···OW	174·7 (24)
	111·0 (3)		178·1 (34)
HA31—CA3—HA32	106·4 (3)	OA1^{v}···Na···OB1	95·6 (1)
	106·1 (4)		96·0 (2)
HA31—CA3—CA3′	109·7 (2)	OA1^{v}···Na···OB1^{iv}	96·6 (1)
	109·3 (3)		95·6 (2)
HA31—CA3—CA2	109·8 (2)	OA2···Na···OB1	85·0 (1)
	109·9 (3)		85·4 (2)
HA32—CA3—CA3′	109·2 (2)	OA1···Na···OB1^{iv}	166·2 (2)
	109·0 (3)		166·0 (2)
HA32—CA3—CA2	109·1 (2)	OA2···Na···OA1^{ii}	79·6 (1)
	109·7 (3)		79·5 (2)
		OA2···Na···OA1^{v}	90·8 (1)
			91·4 (2)

(*c*) Torsion angles

OA1—CA1—CA2—CA3	51·9 (2)	CA2—CA3—CA3′—CA2′	180·0 (1)
	53·7 (3)		180·0 (2)
OA2—CA1—CA2—CA3	− 128·3 (1)	HA—OA2—CA1—OA1	− 0·1 (2)
	− 126·9 (2)		− 0·3 (3)
CA1—CA2—CA3—CA3′	177·3 (1)	HA—OA2—CA1—CA2	− 179·9 (1)
	177·1 (2)		− 179·7 (2)

Symmetry code: (i) x, y, z; (ii) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (iii) $-x, y, -z$; (iv) $-x, 1-y, -z$; (v) $-\frac{1}{2}+x, \frac{1}{2}-y, z$; (vi) $x, -y, z$; (vii) $\frac{1}{2}+x, \frac{1}{2}-y, z$.

Short hydrogen bonds have often been observed in crystal structures of acid salts of mono- and dicarboxylic acids. According to the classification of Currie & Speakman (1970), the presently described structure is of type *A* because there are chains with indistinguishable adipates linked by symmetric hydrogen bonds. A similar type-*A* crystal structure was found for sodium hydrogen succinate (McAdam, Currie & Speakman, 1971), with an O···O distance of 2·444 (9) Å at 295 K. In type-*B* crystal structures, such as potassium hydrogen diformate (Hermansson, Tellgren & Lehmann, 1983), where the O···O distance is 2·437 (1) Å at 120 K, the two O—H bonds are not symmetry equivalent. In this structure, neutron diffraction data showed that the O—H distances were significantly different [1·167 and 1·270 (1) Å].

The water molecule lies in a special position with a mirror plane bisecting the H*W*—O*W*—H*W* angle [107·1 (5)° at 220 K]. The O*W*—H*W* bond length is 0·936 (5) Å. The water molecule forms two equivalent hydrogen bonds O*W*—H*W*···O*A*1 with H···O distances 1·81 Å and O—H···O angles 171·6 (4)°. It is also an acceptor for a third hydrogen bond O*B*2—H*B*···O*W* formed in the mirror plane and having an H···O distance of 1·705 (3) Å and O—H···O angle of 175 (2)°. The three hydrogen bonds make almost regular tetrahedral angles at the water O*W*. Other near neighbours of O*W* are a second water molecule lying on the same mirror plane with O···O distance 3·373 (4) Å and the methylene H*A*31 atoms of two different hydrogen adipate chains [H···O distances 2·902 (4) Å]

The Na ion occupies a special position on a two-fold rotation axis and is octahedrally coordinated with O atoms. The three distinct Na···O distances, 2·38, 2·390 and 2·424 (4) Å at 220 K, are within the range of those observed in other sodium carboxylates (Olovsson, Olovsson & Lehmann, 1984; Delaplane, Tellgren & Olovsson, 1984). The Na cations (Fig. 5) contribute to the crosslinking of hydrogen adipate chains and adipic acid molecules.

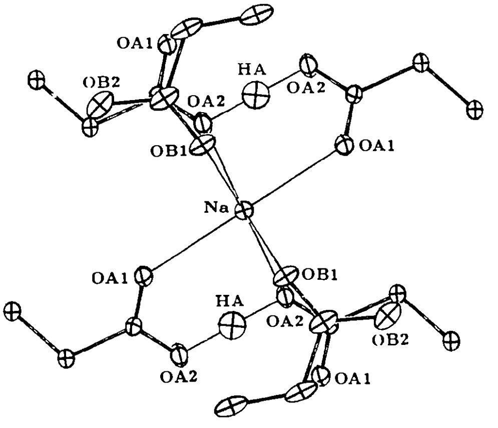

Fig. 5. The environment of the Na cations with thermal ellipsoids at the 20% level of probability (Johnson, 1976).

The adipic acid molecule (*B*) occupies a special position with symmetry 2/*m*. The long axis of the adipic acid molecule is along the direction [30$\bar{2}$], making an angle 49° with the hydrogen adipate chains. The adipic acid interatomic distances and angles (Table 3) have limited physical significance in terms of bond lengths and angles because they are obtained from the positions of the nuclei averaged over unusually large displacements involving both thermal vibrations and disorder.

Thermal vibrations and disorder

A helpful approach for deciding whether the nuclei of the adipic acid molecule are disordered or undergoing large-amplitute thermal vibrations comes from a comparison of the anisotropic thermal parameters at 220 and 295 K. At temperatures high enough that classical theory is obeyed, the mean-square amplitudes of nuclear thermal vibrations should be proportional to the absolute temerpature. This would predict that U_{ii} (220 K) should be 0·745U_{ii} (295 K). With values obtained from the refinement assuming harmonic vibrations, we find agreement with classical theory within experimental error for the Na cation, the water molecule and for the nuclei of the hydrogen adipate chains, including the H atoms. The most significant difference is for O*W* where U_{11} (220 K) is observed to be smaller than predicted by 0·009 (4) Å^2. Similar agreement is obtained for most nuclei of the adipic acid molecule *B*. However, U_{22} values are observed to be larger than predicted by amounts which are marginally significant for C*B*2 [0·016 (6) Å^2] and highly significant for H*B*2 and H*B*3 [0·122 (25) and 0·086 (22) Å^2 respectively]. This is an indication that the mean-square displacements U_{22} for these nuclei may arise in part from disorder.

Kuhs (1983) has pointed out the advantages of using anharmonic p.d.f.'s to describe nuclear mean-square displacements which are the result of averaging both over time with respect to thermal vibrations and over space with respect to disorder. The p.d.f.'s at 220 K for the adipic acid methylene groups are shown in Fig. 6, these being the nuclei with the largest high-order terms in the Gram–Charlier expansion to fourth order. It should be noted that H*B*2 and H*B*3 have bimodal p.d.f.'s and can therefore be regarded as disordered. The disorder must also involve C*B*2 and C*B*3 but the alternative sites are unresolved. Unfortunately, the anharmonic p.d.f.'s are so diffuse that we were unable to identify the individual conformers of the disordered adipic acid molecule. We conclude that the adipic acid molecule, when fully extended, is somewhat longer than is required for its role in the bridging of Na cations. The carboxylate groups at each end of the molecule are held by strong interactions so that some compressional strain is transmitted to the hydrocarbon chain, thus resulting in conformational disorder.

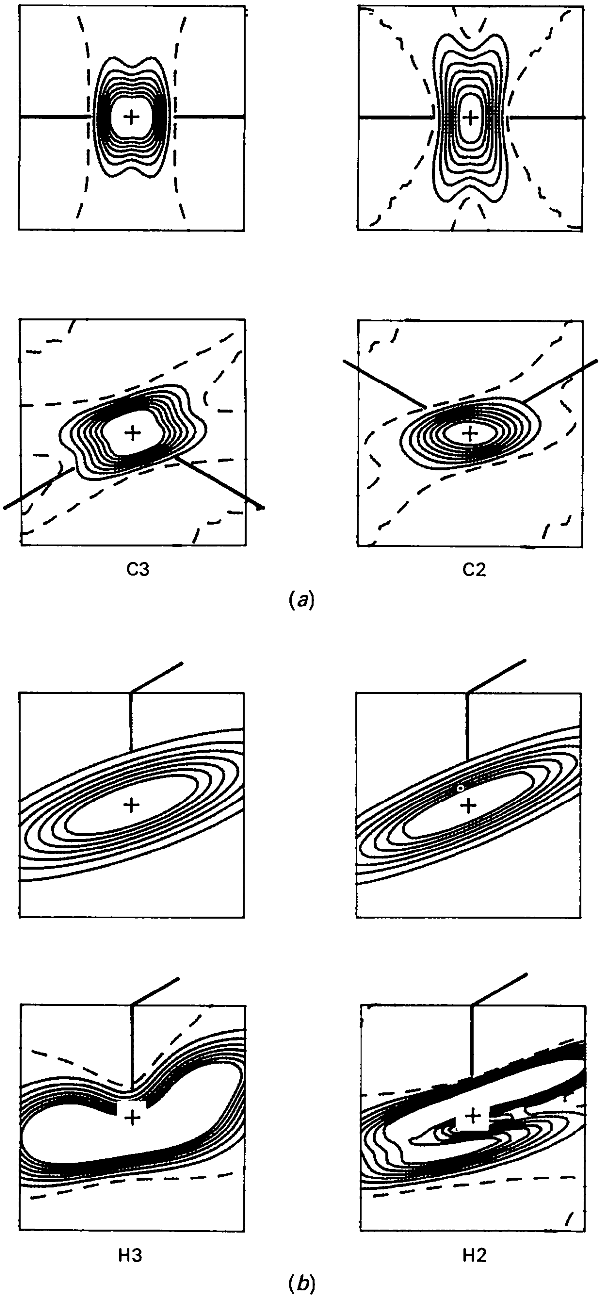

Fig. 6. Sections through the probability density functions (p.d.f.'s) at 220 K for the nuclei of the adipic acid methylene groups (Craven, He & Weber 1985). The sections measure 2 × 2 Å. The zero contour is shown dashed. Negative excursions in the p.d.f.'s are not significant. The third highest contour is at 50% probability for enclosing the nucleus. (*a*) Total p.d.f.'s up to fourth order in the Gram–Charlier expansion for the C nuclei. C*B*3 is shown on the left and C*B*2 on the right. Lines are drawn to indicate the crystallographic mirror plane (upper sections) and the C—C bonds (lower sections). (*b*) Sections for the H nuclei in the plane of the CH_2 group. H*B*3 is shown on the left and H*B*2 on the right. In both cases, the upper section is the Gaussian p.d.f. from the refinement based on the harmonic model. The lower section is the total p.d.f. after the later refinement based on the anharmonic model.

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