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Nickel Dihydrogen Diphthalate Hexahydrate

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Abstract. $NiH_2(C_8O_4H_4)_2.6H_2O$, monoclinic, space group $P2_1/c$, $a=16{\cdot}024$ (2), $b=5{\cdot}574$ (1), $c=12{\cdot}500$ (2) Å, $\beta=113{\cdot}42$ (2)° (measured at 18 °C), $Z=2$, $D_x=1{\cdot}611$ g cm^{-3}. The structure has been solved by direct methods and refined to $R=0{\cdot}030$ for 1619 independent observed reflexions. There is a nearly regular octahedral coordination around the Ni ion, Ni–O ranging between 2·036 and 2·095 Å. These octahedra and the hydrogen phthalate ions are linked by hydrogen bonds to form a layer-like structure parallel to (100).

Introduction. Gonschorek & Küppers (1975) reported the structure of lithium hydrogen phthalate dihydrate where the hydrogen phthalate ion forms a very short intramolecular hydrogen bond (2·385 Å). We are now investigating further acid phthalates to see if they form similarly short hydrogen bonds. High H_2O content and low coordination number of the cation should favour such a geometry.

Acid nickel phthalate was first described by Cingi & Magnano (1959), who determined the lattice parameters from Weissenberg photographs as $a=15{\cdot}94$, $b=5{\cdot}60$, $c=12{\cdot}47$ Å, $\beta=112{\cdot}4°$.

Small plate-like crystals were prepared by slow evaporation of a stoichiometric aqueous solution. Intensities from a crystal of approximate dimensions 0·4 × 0·3 × 0·1 mm were collected on an automatic Hilger–Watts Y 290 diffractometer with Mo $K\alpha$ radiation. All reflexions with scattering angle $\theta<26°$ were measured and 1806 independent $|F_o|$ values were obtained. No absorption correction was applied ($\mu=9{\cdot}6$ cm^{-1}).

The structure was solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). A first attempt failed because the Ni atom occupies a special position (with inversion symmetry $\bar{1}$), thus forming an A-centred lattice. Therefore, the largest E values belong to parity groups which are not affected by the extinction rules due to A-centring. After a separate appropriate scale factor was applied to reflexions in each of the eight parity groups the program yielded a solution.

Further calculations were done with the X-RAY 70 System (Stewart, Kundell & Baldwin, 1970). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Full-matrix refinement of the non-hydrogen atoms with anisotropic temperature factors resulted in an R value of 0·071. The $|F_o|$ values were weighted with the reciprocal standard deviation of the respective F_o calculated from counting statistics. A difference Fourier map then clearly revealed the positions of the hydrogen atoms. Subsequent refinement with isotropic temperature factors for the hydrogens and omitting 187 'less-thans' ($|F_o|<2\sigma$) led to $R=0{\cdot}030$. Final positional and thermal parameters are given in Table 1. Since only reflexions of lower order with respect to the second

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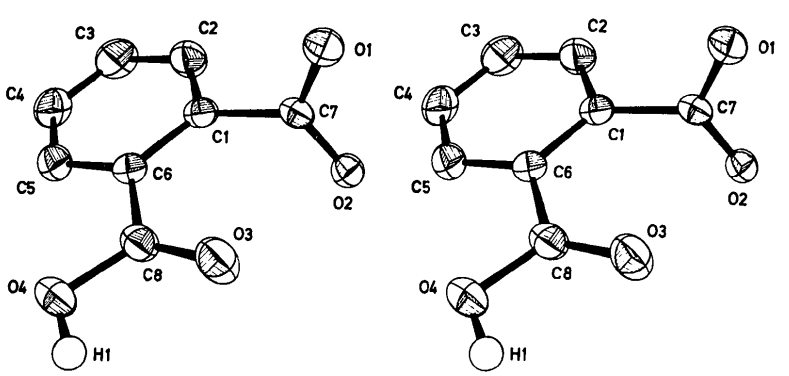

Fig. 1. Stereoscopic thermal ellipsoid plot of the hydrogen phthalate ion (*ORTEP*; Johnson, 1965).

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and thermal parameters* β_{ij} ($\times 10^5$) (*or B*)

Standard deviations given in parentheses refer to the least significant digits in the parameter values. The temperature factor is of the form $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\times 10^{-5}]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	5000	5000	5000	215 (3)	1306 (19)	315 (4)	−25 (8)	127 (3)	55 (11)
C(1)	2108 (2)	3747 (6)	4020 (3)	221 (15)	1918 (121)	310 (24)	−32 (33)	68 (15)	87 (45)
C(2)	1710 (2)	1918 (7)	3250 (3)	343 (18)	3036 (158)	490 (30)	−191 (42)	174 (19)	−357 (57)
C(3)	940 (3)	769 (7)	3238 (3)	390 (20)	2988 (166)	651 (35)	−385 (43)	110 (22)	−411 (59)
C(4)	565 (2)	1466 (7)	4011 (3)	271 (18)	3190 (163)	664 (34)	−354 (43)	139 (20)	49 (61)
C(5)	957 (2)	3299 (7)	4782 (3)	261 (17)	2880 (153)	509 (31)	19 (39)	182 (19)	206 (55)
C(6)	1724 (2)	4485 (5)	4798 (2)	214 (13)	1855 (146)	316 (22)	45 (31)	86 (14)	78 (41)
C(7)	2964 (2)	4819 (7)	3992 (2)	261 (14)	1000 (117)	303 (21)	−55 (43)	144 (14)	−61 (56)
C(8)	2161 (2)	6435 (6)	5649 (3)	288 (16)	2071 (129)	378 (26)	53 (37)	161 (17)	113 (48)
O(1)	2883 (1)	6324 (5)	3219 (2)	286 (12)	3439 (105)	456 (20)	3 (28)	140 (12)	516 (39)
O(2)	3709 (1)	3972 (4)	4710 (2)	236 (11)	2024 (82)	408 (18)	−44 (23)	131 (12)	226 (32)
O(3)	2859 (2)	7424 (4)	5760 (2)	400 (13)	2569 (98)	582 (21)	−326 (29)	299 (14)	−397 (38)
O(4)	1696 (2)	6969(5)	6297 (2)	335 (13)	3498 (119)	446 (21)	−120 (31)	219 (14)	−404 (42)
O(5)	5072 (2)	2517 (4)	3782 (2)	354 (14)	1944 (92)	466 (23)	−22 (32)	203 (15)	−100 (37)
O(6)	4578 (2)	7566 (5)	3707 (2)	291 (13)	1959 (101)	510 (21)	−62 (31)	151 (13)	158 (38)
O(7)	3634 (2)	2019 (7)	6790 (3)	521 (17)	3236 (137)	472 (24)	−218 (35)	176 (17)	272 (47)

Table 1 (*cont.*)

	x	y	z	B(Å^2)
H(1)	2017 (25)	7754 (73)	6820 (32)	4·21 (1·10)
H(2)	1953 (21)	1409 (61)	2722 (28)	3·32 (80)
H(3)	665 (22)	−576 (63)	2690 (29)	3·63 (85)
H(4)	20 (23)	671 (65)	3995 (30)	4·57 (90)
H(5)	731 (22)	3770 (63)	5311 (29)	3·44 (83)
H(51)	4638 (24)	2732 (68)	3151 (32)	3·44 (97)
H(52)	5591 (26)	2768 (71)	3811 (31)	6·04 (99)
H(61)	3999 (28)	7455 (79)	3468 (34)	5·29 (1·13)
H(62)	4804 (22)	9044 (65)	3894 (29)	2·96 (84)
H(71)	3482 (35)	408 (121)	6584 (48)	10·10 (1·82)
H(72)	3660 (35)	2404 (101)	6318 (44)	7·01 (1·82)

Miller index k were measured (b is comparatively small) the standard deviations of y and β_{22} are rather large.*

Discussion. Fig. 1 shows a stereoscopic view of the hydrogen phthalate ion. The heavy atoms are represented by their thermal ellipsoids which are scaled to contain 50% probability of space occupancy. The H atom is drawn with an arbitrary temperature factor of $B=1{\cdot}5$. Evidently, the ion does not form a planar configuration nor a short intramolecular hydrogen bond as found in $LiH(C_8O_4H_4).2H_2O$. The least-squares plane P_1 for atoms C(1) to C(8) is described by the following

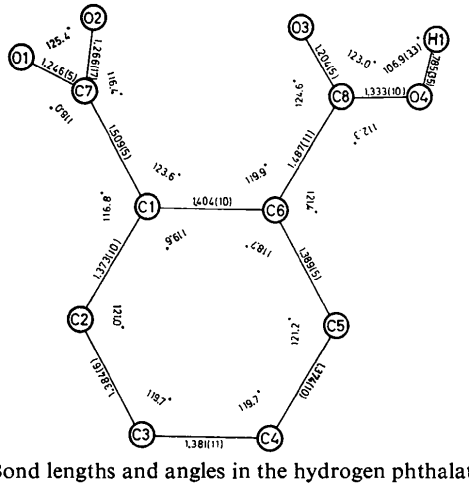

Fig. 2. Bond lengths and angles in the hydrogen phthalate ion.

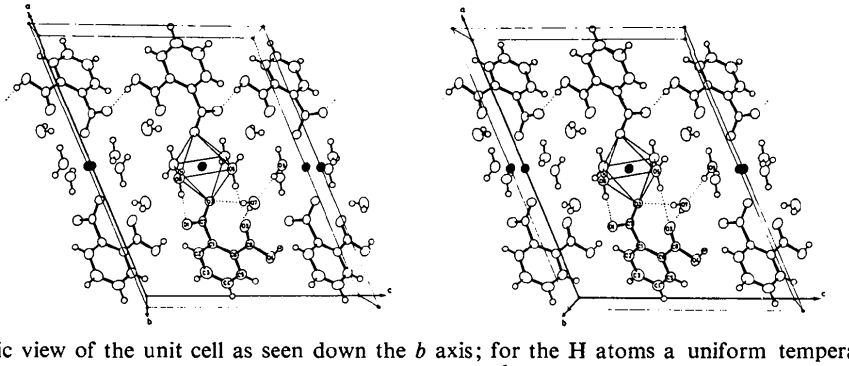

Fig. 3. Stereoscopic view of the unit cell as seen down the b axis; for the H atoms a uniform temperature factor $B=0{\cdot}8$ Å^2 was assumed.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31630 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

equation (as related to a Cartesian coordinate system with $x\|\mathbf{a}$, $y\|\mathbf{b}$, $z\|\mathbf{c}^*$):

$$0{\cdot}329x-0{\cdot}665y+0{\cdot}670z=2{\cdot}169\ .$$

The maximum deviation from this plane is 0·024 Å. Planes P_2 [C(7), O(1), O(2)] and P_3 [C(8), O(3), O(4)] have the following equations respectively:

$$-0{\cdot}212x+0{\cdot}739y+0{\cdot}639z=4{\cdot}325$$
$$0{\cdot}276x-0{\cdot}688y+0{\cdot}671z=2{\cdot}061\ .$$

P_2 and P_3 make angles of 82·4 and 3·2°, respectively, with P_1.

Distances and angles in the hydrogen phthalate ion are given in Fig. 2. All values are within the usual range. The standard deviations of angles are 0·3°.

The Ni ion occupies a special position with symmetry $\bar{1}$ and is coordinated by six oxygens which form a fairly regular octahedron as outlined in Fig. 3 [Ni–O(2)=2·036 (8), Ni–O(5)=2·095 (3), Ni–O(6)=2·061 (11) Å]. The O–Ni–O angles range between 87 and 93°. The lengths of the edges of the octahedron are (a prime denotes atoms generated by inversion at the Ni atom):

O(2)–O(5) 2·965 (18) Å	O(5)–O(6′) 2·962 (12) Å
O(2)–O(6) 2·986 (12)	O(5)–O(2′) 2·877 (26)
O(5)–O(6) 2·915 (4)	O(2)–O(6′) 2·805 (39)

The packing of the molecules and the coordination octahedra in the lattice are illustrated in Fig. 3. The Ni ion provides an ionic contact between two hydrogen phthalate ions *via* O(2) and O(2′). Further linkage is mainly achieved by a complicated framework of seven hydrogen bonds which are listed in Table 2 and denoted in Fig. 3 by dashed and dotted lines. The hydrogen phthalate ions are mutually interconnected by strong (dashed) hydrogen bonds (2·581 Å) between O(4) and O(1), thus forming infinite chains in the [001] direction. The coordination octahedra are linked in the **b** direction by hydrogen bonds (2·862 Å) which connect edges O(5)–O(6) with edges O(5)–O(6″) of the neighbouring cell above or below the cell drawn in Fig. 3 *via* H(62) and H(62′). One of the latter is denoted by H in Fig. 3.

Table 2. *Distances* (Å) *and angles* α *of the hydrogen bonds*

D–*H*···*A*	*D*···*A*	H–*D*	H···*A*	α
O(4)–H(1)···O(1)	2·581 (36)	0·784	1·822	162°
O(5)–H(51)···O(7)	2·649 (43)	0·827	1·824	175
O(5)–H(52)···O(3)	3·133 (13)	0·829	2·326	164
O(6)–H(61)···O(1)	2·629 (13)	0·857	1·802	162
O(6)–H(62)···O(5)	2·862 (4)	0·892	2·000	162
O(7)–H(71)···O(3)	2·914 (12)	0·939	2·001	163
O(7)–H(72)···O(2)	2·865 (5)	0·645	2·221	176

The structural configuration of the crystal may be described, therefore, as follows: the Ni ions which lie on (100) planes at $x=0{\cdot}5$ are surrounded by oxygens, forming layers extending in the **b** and **c** directions. On each side, hydrogen phthalate ions are attached to this layer, turning their carboxylic groups towards the Ni layer. The interconnexion within such a threefold layer is quite strong. Between them, however, *i.e.* along planes like that formed by *b* and *c* (Fig. 3), only poor cohesion exists. Along these planes the benzene rings touch and linkage is caused merely by van der Waals forces. Conseqently, the crystal exhibits a marked cleavage parallel to (100). Furthermore, (100) predominates in the morphology of the crystals grown from aqueous solution.

Whereas the two water molecules O(5) and O(6) are held in a rigid position by their contact to the Ni ion, water molecule O(7) is linked only by hydrogen bonds. Consequently, its position is less well defined and its temperature factors and those of H(71) and H(72) are higher than the average of those for the other atoms.

Since it must be supposed that the COO groups librate independently around the C–C bond, a rigid-body treatment (Schomaker & Trueblood, 1968) was performed using the relatively rigid framework of eight C atoms. The O atoms were taken into account, however, in the evaluation of the molecules' centre of gravity. Thus the following principal components of **L** tensor (in deg²) and **T** tensor (in Å²) were obtained. (Standard deviations are given in parentheses and these are followed by the direction cosines of the particular principal axis as referred to the Cartesian system as defined above.)

$L_1=22{\cdot}0$ (4·7)	0·826	0·477	0·301
$L_2=\ 8{\cdot}2$ (2·8)	0·121	−0·684	0·719
$L_3=\ 4{\cdot}1$ (2·0)	0·551	−0·566	−0·613
$T_1=0{\cdot}028$ (2)	0·032	0·939	0·343
$T_2=0{\cdot}025$ (1)	0·997	−0·050	0·058
$T_3=0{\cdot}017$ (2)	0·071	0·340	−0·938

The effective screw translations parallel to the respective **L** axes are: 0·004, 0·008, −0·020 Å. The estimated standard deviation of the U_{ij} is 0·0023.

Whereas the translational motion is rather uniform, the librational motion of the molecule takes place preferentially about the principal axis L_1. In order to visualize the topological situation, it should be noted that this principal axis is oriented nearly parallel to the line defined by C(2) and C(3) (direction cosines 0·886; 0·462; 0·010) and that the principal axis L_2 is oriented nearly along the normal to the least-squares plane through the C atoms (direction cosines 0·329; −0·665; 0·670).

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N-Acetyl-L-tyrosine-*p*-nitroanilide

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Abstract. $C_{17}H_{17}N_3O_5$; M.W. 343·34; orthorhombic, space group $P2_12_12_1$; $a=15{\cdot}621$, $b=19{\cdot}941$, $c=5{\cdot}253$ Å; $D_m=1{\cdot}394$, $D_c=1{\cdot}393$ g cm^{-3} for $Z=4$. $R=0{\cdot}058$ for 1496 observed reflexions. The structure is compared with that of acetyltyrosine ethyl ester.

Introduction. The crystal was colourless and cut into a needle elongated on b ($0{\cdot}2\times0{\cdot}2\times0{\cdot}4$ mm). The space group was determined from precession photographs and confirmed on a CAD-4 Nonius automatic diffractometer. 1905 reflexions were measured with Cu $K\alpha$ radiation by the ω–2θ scan method. One standard intensity was counted every 50 reflexions. No fluctuation was observed. In the range $2\theta\leq140°$, 1496 reflexions had intensities greater than $2{\cdot}5\sigma$ above background, where $\sigma(I)$ is defined by $\sigma^2(I)=S+B+(0{\cdot}03S)^2$, S being the scan and B the background count. Lorentz and polarization factors were applied, but no absorption correction. E statistics confirmed the non-centrosymmetric space group. The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). Phases of 240 E's with $|E|\geq1{\cdot}4$

Table 1. *Parameters derived from the final least-squares refinement* (*all* $\times10^4$)

The expressions used for the temperature factors are:

$\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$ and $\exp[-2\pi^2U(2\sin\theta/\lambda)^2]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	1177 (3)	4044 (2)	9412 (9)	699 (28)	347 (20)	578 (26)	68 (19)	−166 (25)	−78 (20)
O(2)	2176 (3)	3140 (2)	1963 (9)	610 (27)	637 (28)	446 (26)	100 (21)	−73 (24)	67 (24)
O(3)	8634 (3)	3168 (2)	1472 (8)	1174 (37)	345 (20)	314 (22)	−222 (23)	−43 (26)	53 (18)
O(4)	5983 (5)	3510 (2)	8671 (18)	1593 (65)	391 (28)	1726 (78)	−20 (34)	−750 (66)	−213 (40)
O(5)	6579 (5)	3498 (2)	2279 (18)	1722 (71)	462 (30)	1337 (65)	224 (36)	−249 (63)	285 (40)
N(1)	2452 (2)	2838 (2)	5998 (9)	373 (24)	349 (22)	403 (26)	38 (18)	17 (21)	50 (22)
N(2)	8652 (3)	3395 (2)	5714 (8)	516 (25)	307 (20)	273 (22)	−28 (19)	23 (21)	36 (18)
N(3)	6279 (3)	3788 (2)	478 (16)	558 (31)	333 (27)	933 (50)	20 (24)	63 (36)	70 (34)
C(1)	1208 (3)	4700 (2)	173 (10)	462 (27)	319 (24)	358 (28)	12 (21)	−4 (24)	−27 (22)
C(2)	760 (3)	5157 (2)	8698 (11)	427 (27)	399 (26)	413 (29)	−25 (23)	−49 (26)	12 (26)
C(3)	4260 (3)	4175 (2)	4393 (12)	438 (30)	379 (26)	445 (30)	18 (23)	74 (28)	−39 (26)
C(4)	3837 (3)	3947 (2)	6558 (11)	374 (25)	326 (25)	433 (30)	−13 (20)	−46 (26)	16 (23)
C(5)	3376 (3)	4410 (2)	7976 (12)	458 (30)	395 (28)	389 (31)	−38 (24)	15 (27)	27 (26)
C(6)	1648 (3)	4914 (2)	2310 (12)	543 (32)	367 (27)	408 (31)	62 (23)	−84 (29)	11 (25)
C(7)	3902 (3)	3221 (2)	7344 (12)	470 (31)	337 (28)	516 (32)	3 (22)	−107 (28)	58 (26)
C(8)	3372 (3)	2747 (2)	5657 (11)	483 (32)	291 (22)	387 (28)	94 (21)	27 (25)	63 (22)
C(9)	1917 (3)	2996 (2)	4125 (13)	479 (33)	253 (24)	523 (38)	1 (23)	−22 (31)	−34 (25)
C(10)	977 (3)	3007 (3)	4764 (16)	336 (28)	684 (39)	767 (49)	6 (28)	−24 (31)	−107 (38)
C(11)	8569 (3)	2983 (2)	3677 (11)	466 (30)	338 (27)	394 (32)	−82 (24)	−46 (28)	86 (24)
C(12)	8709 (3)	4099 (2)	5609 (11)	357 (28)	326 (24)	303 (27)	−17 (22)	−21 (25)	24 (24)
C(13)	8328 (3)	4458 (2)	7589 (11)	468 (30)	442 (28)	380 (27)	−4 (23)	49 (27)	0 (25)
C(14)	6672 (3)	4846 (3)	2577 (12)	428 (30)	487 (30)	463 (32)	85 (25)	−1 (29)	74 (30)
C(15)	6263 (3)	4526 (2)	583 (12)	447 (29)	293 (23)	545 (33)	−10 (21)	50 (28)	64 (25)
C(16)	5851 (3)	4867 (2)	8650 (12)	456 (28)	367 (28)	502 (31)	−80 (24)	−4 (28)	−6 (26)
C(17)	9135 (3)	4434 (2)	3651 (11)	405 (26)	346 (23)	398 (28)	−46 (21)	58 (26)	−31 (24)