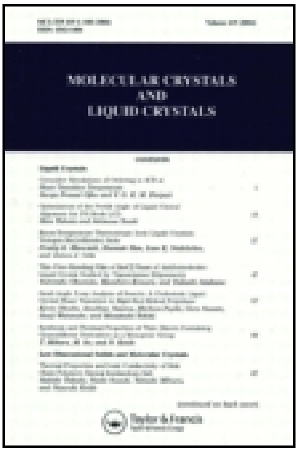

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The Solid State Chemistry and Polymorphism of Aquomagnesium Hydrogen Phthalates

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THE SOLID STATE CHEMISTRY AND POLYMORPHISM OF AQUOMAGNESIUM HYDROGEN PHTHALATES

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Abstract. Five crystalline phases of magnesium hydrogen phthalate are described. The structures contain two, six or eight molecules of water per cation. Full crystal structures of two of the series (di-aquomagnesium hydrogen phthalate and hexa-aquomagnesium hydrogen phthalate) are reported and some general features of all the hydrogen phthalates are discussed.

Di-aquomagnesium hydrogen phthalate: $Mg^{2+}.2C_8O_4H_5^-.2H_2O$, $M_r = 390.60$, monoclinic, $P2_1/c$, $a = 12.916(1)$, $b = 5.092(1)$, $c = 12.956(2)$ Å, $\beta = 113.98(1)°$, $V = 778$ Å^3, $Z = 2$, $D_x = 1.66$ g cm^{-3}, λ(Mo K$_\alpha$) = 0.71069 Å, $\mu = 1.24$ cm^{-1}, F(000) = 400, T = 295 K, R = 0.058 for 967 observed reflections.

Hexa-aquomagnesium hydrogen phthalate: $Mg^{2+}.(C_8O_4H_5^-)_2.6H_2O$ $M_r = 462.65$, monoclinic, C2/m, $a = 16.674(3)$, $b = 9.811(2)$, $c = 6.288(2)$ Å, $b = 98.20(2)°$, $V = 1\,018.0$ Å^3, $Z = 2$, $D_x = 1.50$ g cm^{-3}, λ(Mo Kα) = 0.71069 Å, $\mu = 1.13$ cm^{-1}, F(000) = 480.0, T = 295 K, R = 0.033 for 681 observed reflections.

Keywords: polymorphism, magnesium phthalates, crystal structures, di-aquomagnesium hydrogen phthalate, hexa-aquomagnesium hydrogen phthalate

INTRODUCTION

Magnesium monoperoxyphthalate hexahydrate (MMPP) has received interest as a potential bleaching agent.[1] We have reported earlier[2] on the solid-state decomposition of this material and have indicated that an extensive range of polymorphic forms exist of the decomposition product. In this paper we discuss the various polymorphs of magnesium hydrogen pthalate which have been observed as well as the procedures for obtaining them. It has been important for us to determine the structures of the various forms in order to know more of the crystallographic relationships which exist between the reactant and the various solid state products. We have reported previously on the structure of three polymorphs[3,4] and the structural relationship between the peracid and the acid salts.[4]

EXPERIMENTAL

Structure determinations

Di-aquomagnesium hydrogen phthalate (**D**): The crystal used (0.1 x 0.2 x 0.3 mm) was obtained after stoichiometric amounts of magnesium oxide and phthalic acid were mixed (mole ratio of 1:2) and dissolved in hot water. The solvent was allowed to evaporate at 85°C to yield crystals of **D**.

Lattice parameters were refined using 25 reflections in the range $9 \leq \theta \leq 15°$. An Enraf-Nonius CAD-4 four-circle diffractometer in the $\omega/2\theta$ scan mode with graphite monochromated Mo radiation was used. A total of 967 observed X-ray intensities ($F>3\sigma(F)$) were recorded in the range $1.5 \leq \theta \leq 30°$ (index range *h* 0/18, *k* 0/7, *l* -18/18). Standard reflections (0 0 6), $(0\ 0\ \bar{6})$ and $(6\ 0\ \bar{6})$ were recentered every 100 reflections and scanned every 3 hours to check for movement and stability of the crystal. No significant deviations were observed. The structure was solved by direct methods using SHELXS84[5] and refined by full-matrix least squares analysis using SHELX76[5]. The positions of the ring hydrogen atoms were fixed geometrically. All non-hydrogen atoms were assigned anisotropic thermal parameters to give an R-value of 0.058. The difference Fourier synthesis map revealed the locations of the carboxylic and water hydrogens. In the final cycle of refinement the maximum shift/e.s.d. was 0.186. The maximum and minimum heights in the final difference Fourier synthesis map were 0.42 and -0.40 electrons $Å^{-3}$ respectively. Atomic scattering factors from *International Tables for X-ray Crystallography*[7] were used.

Hexa-aquomagnesium hydrogen phthalate (**H**): A suitable crystal (0.4 x 0.2 x 0.1 mm) was obtained by the slow evaporation (at 20°C) of a solution of magnesium hydrogen phthalate in methanol. Lattice parameters were refined using 25 reflections in the range $10 \leq \theta \leq 15°$. A total of 681 observed X-ray intensities ($F>6\sigma F$) were recorded in the range $1.5 \leq \theta \leq 25°$ (index range h 0/19, k 0/11, l -7/7). Standard reflections (8 0 2), (6 2 $\bar{2}$) and (6 0 $\bar{3}$) were recentered every 100 reflections and scanned every 3 hours to check for movement and stability of the crystal. No significant deviation was observed. Structure solution and refinement was as described for **D**. The difference Fourier synthesis map revealed the positions of the ring carboxylic and water hydrogen atoms. The final R-value was 0.033. In the final cycle of refinement the maximum shift/e.s.d. was 0.240. The maximum and minimum heights in the final difference Fourier synthesis map were 0.20 and -0.23 electrons $Å^{-3}$ respectively. Crystal structures were viewed using PLUTO[6] and the Cerius Molecular Structures package.[6]

Structure-factor listings, anisotropic thermal parameters, H-atom positions and complete molecular geometry for both structures have been deposited with the British Library Document Supply Centre as Supplementary Publication No. 90248. Copies may be obtained through Customer Services, The British Library, Document Supply Centre, Boston Spa, Wetherby, West Yorkshire LS23 7BQ, United Kingdom

Powder X-ray diffraction

A Philips PW1710 powder diffractometer was used to obtain powder X-ray diffraction data. About 0.5 gram of sample was ground and placed on a glass holder. The data were collected at room temperature using the θ-2θ technique and Cu Kα radiation (λ = 1.5418 Å) at a scan rate of 2°/minute in 2θ.

Thermogravimetric analysis

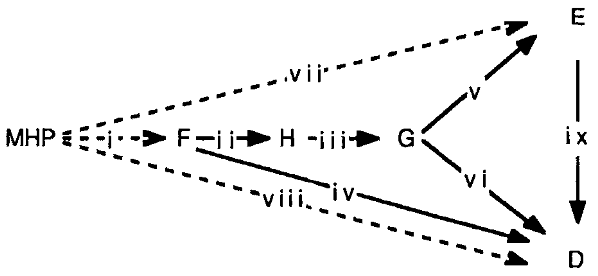
Thermogravimetric analysis was performed using a Stanton Redcroft TG-770 instrument under a stream of nitrogen. The weight of the sample (usually less than 10 mg) was recorded with a temperature ramp of 3°/minute.

Heating and rehydration of samples

Heating was carried out in a Gallenkamp vacuum oven in air. The samples were exposed to moisture by placing them on a petri dish next to a 50 cm^{-3} beaker containing water. These were then covered with a 500 cm^{-3} beaker and left to stand.

Interconversion of polymorphs

Scheme 1 summarises the range of procedures used to produce the various polymorphs.



SCHEME 1

MHP - Solution of magnesium hydrogen phthalate in water
D - $Mg(H_2O)_2(O_2CC_6H_4CO_2H)_2$
E,H - $Mg(H_2O)_6(O_2CC_6H_4CO_2H)_2$
F - $Mg(H_2O)_6(O_2CC_6H_4CO_2H)_2(H_2O)_2$
G - $Mg(O_2CC_6H_4CO_2H)_2$

The designation of the various phases is shown in this Scheme. (The formulae indicated are based on the various results which we have obtained and are discussed in the text). Specific details are as follows:

i) Recrystallization of magnesium hydrogen phthalate from aqueous solution (MHP) at room temperature yielded a crystalline solid - designated **F**.

ii) Partial dehydration of **F** by controlled heating at 60°C resulted in the crystalline phase **H**.

iii) Complete dehydration of **F** (through the phase **H**) by heating in the open at 70°C resulted in the amorphous phase **G**.

iv) The heating of **F** above 80°C in water vapour or in a sealed container resulted in the crystalline phase **D**.

v) Crystalline **E** was obtained by exposing **G**, which was amorphous, to water vapour at 20°C.

vi) Exposure of **G** to water vapour above ~80°C gave the phase **D**.

vii) Recrystallization of magnesium hydrogen phthalate from water (MHP) between ~50 and 80°C resulted in crystals of phase **E**.

viii) Phase **D** was also obtained by the recrystallization of magnesium hydrogen phthalate from aqueous solution (MHP) above 80°C.

Microanalysis results for some of the various phases are presented in Table 1.

TABLE 1: Microanalytical data (% Obtained/Expected) based on the formuale given in Scheme 1 and in the text.

	C	H
E	38.3/41.6	5.1/4.8
F	38.8/38.6	5.1/5.2
G	53.0/54.2	2.9/2.8
H	42.4/41.6	4.7/4.8
I	61.6/64.9	2.8/2.7
J	50.0/51.1	2.7/2.1

A further crystalline phase of magnesium hydrogen phthalate, $[Mg(H_2O)_6(O_2CC_6H_4CO_2H)_2$, designated **C**, has also been obtained and is described elsewhere.[2,4]

RESULTS AND DISCUSSION

Structure of di-aquomagnesium hydrogen phthalate (D)

The structure of **D** is composed of magnesium cations, hydrogen phthalate anions and water molecules. Atomic fractional parameters are given in Table 2. Bond lengths and angles are presented in Table 3. The atom numbering scheme for the anion is shown in Figure 1.

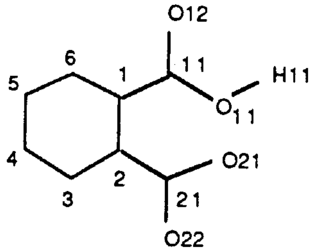


FIGURE 1. Anion atom numbering scheme for di-aquomagnesium hydrogen phthalate (**D**)

The Mg^{2+} ions lie on centres of symmetry. Each is surrounded by six oxygen atoms, two of which are from water molecules and four from neighbouring anions. They form distorted octahedra around the cations (Table 4) with a mean Mg - O distance of 2.085(4) Å. Oxygen atoms from the anions are involved in coordination with Mg^{2+} in other structures such as $Mg(C_5H_7O_2)_2.2H_2O$[8], $Mg(C_3H_3O_4)_2.2H_2O$[9], $MgC_{15}H_9O_6P.5H_2O$[10], $MgC_4H_4O_4.4H_2O$[11], $MgC_4H_4O_5.5H_2O$[12], $Mg(C_9H_8ClO_3)_2.6H_2O$[13], $Mg(CHO_2)_2.2H_2O$[14] and $Mg(CH_3CO_2)_2.4H_2O$[15].

TABLE 2: Fractional atomic coordinates ($x10^4$) and equivalent isotropic temperature factors ($Å^2 x10^3$) with e.s.d's in parenthesis for **D** and **H**. [$U_{eq}=(U_{11}+U_{22}+U_{33})/3$]

Di-aquomagnesium hydrogen phthalate (**D**)

	x	y	z	Ueq
Mg(1)	5000	0	5000	16
O(1)	4877(4)	2003(9)	3580(4)	24
O(11)	7635(4)	4667(9)	4932(4)	24
O(12)	6244(3)	7465(9)	4788(3)	22
O(21)	6577(3)	1568(9)	7804(19)	23
O(22)	6250(3)	2444(8)	6019(17)	18
C(1)	7766(4)	6604(12)	6606(12)	18
C(2)	7624(4)	5006(12)	7404(4)	16
C(3)	8326(5)	5376(12)	8558(5)	23
C(4)	9140(5)	7329(13)	8881(5)	24
C(5)	9267(5)	8931(13)	8075(5)	29
C(6)	8574(5)	8605(12)	6940(5)	23
C(11)	7102(5)	6249(12)	5348(4)	21
C(21)	6755(4)	2860(11)	7057(4)	15

Hexa-aquomagnesium hydrogen phthalate (**H**)

Mg(1)	5000	0	0	33
O(1)	4399(2)	0	2529(4)	46
O(3)	5000	2099(3)	0	45
O(2)	3888(2)	0	7858(4)	43
O(11)	737(1)	1213(2)	7155(3)	41
O(12)	1044(1)	2897(2)	5155(3)	52
C(1)	1482(1)	719(2)	4200(3)	30
C(2)	1926(2)	1381(3)	2787(4)	45
C(11)	1062(2)	1676(2)	5566(4)	35
C(3)	2361(2)	695(3)	1434(4)	50

Table 3: Bond lengths (Å) and angles (°) for **D** and **H**.

Di-aquomagnesium hydrogen phthalate (**D**)

C(21)-O(21)	1.267(6)	C(1)-C(2)	1.385(7)
C(21)-C(2)	1.499(7)	C(3)-C(2)	1.411(6)
C(11)-C(1)	1.512(7)	C(6)-C(1)	1.396(8)
C(4)-C(3)	1.383(8)	C(5)-C(6)	1.386(8)
C(4)-C(5)	1.386(8)	C(11)-O(11)	1.310(6)
C(21)-O(22)	1.255(5)	C(11)-O(12)	1.219(6)

C(6)-C(1)-C(2)	120.4(4)	C(6)-C(1)-C(11)	116.6(5)
C(2)-C(1)-C(11)	123.0(5)	C(3)-C(2)-C(1)	119.3(5)
C(3)-C(2)-C(21)	119.7(5)	C(1)-C(2)-C(21)	121.0(4)
C(2)-C(3)-C(4)	119.9(5)	C(3)-C(4)-C(5)	120.2(5)
C(6)-C(5)-C(4)	120.3(6)	C(1)-C(6)-C(5)	119.7(6)
O(12)-C(11)-C(1)	124.2(5)	O(11)-C(11)-O(12)	124.7(5)
C(1)-C(11)-O(11)	110.7(4)	O(22)-C(21)-O(21)	123.9(5)
O(22)-C(21)-C(2)	116.4(4)	O(21)-C(21)-C(2)	119.7(4)

Hexa-aquomagnesium hydrogen phthalate (**H**)

C(1)-C(1a)	1.411(6)	C(3)-C(2)	1.371(5)
C(2)-C(1)	1.395(5)	C(11)-C(1)	1.510(5)
C(3)-C(3a)	1.364(7)	C(11)-O(12)	1.225(5)
C(11)-O(11)	1.286(5)		

O(11)-H(11)-O(11)	174.9(45)	C(3a)-C(3)-C(2)	119.4(17)
C(1a)-C(1)-C(2)	117.8(3)	C(11)-C(1)-C(1a)	128.4(17)
C(11)-C(1)-C(2)	113.8(3)	C(3)-C(2)-C(1)	122.8(3)
O(12)-C(11)-O(11)	120.6(3)	C(1)-C(11)-O(11)	120.2(3)
C(1)-C(11)-O(12)	119.2(3)		

(a) = x,-y,z (b) = -x,y,-z

Table 4 The magnesium ion environment and some short intermolecular O-O distances (Å) for **D** and **H**.

Di-aquomagnesium hydrogen phthalate (**D**)

O(1)...Mg(1)	2.052(4)Å	O(12)...Mg(1) ...O(1)	88.5(2)°
O(12)...Mg(1)	2.163(4)	O(22)...Mg(1)...O(1)	91.6(2)
O(22)...Mg(1)	2.040(4)	O(12)...Mg(1)...O(22)	90.7(1)

	Distance	SYMM	TX	TY	TZ
O(21)...O(1)	2.705	- 1	1	0	1
O(21)...O(1)	2.856	2	0	0	0
O(11)...O(21)	2.608	2	0	0	- 1

SYMM refers to the symmetry operator: 1= X,Y,Z; 2=X,-Y+0.5,Z+0.5 and TX,TY and TZ are unit cell translations.

Hexa-aquomagnesium hydrogen phthalate (**H**)

Mg(1)-O(2)	2.133(5)Å	O(3)-Mg(1)-O(1)	90.0(3)°
Mg(1)-O(3)	2.077(5)	O(2)-Mg(1)-O(1)	91.0(3)
Mg(1)-O(1)	1.997(5)	O(2)-Mg(1)-O(3)	90.0(3)

	Distance	SYMM	TX	TY	TZ
O(3)---O(11)	2.842	2	0.5	0.5	- 1
O(3)---O(11)	2.842	- 1	0.5	0.5	1
O(1)---O(12)	2.689	- 1	0.5	0.5	1
O(1)---O(12)	2.689	- 2	0.5	-0.5	1
O(2)---O(12)	2.814	- 1	0.5	0.5	1
O(2)---O(12)	2.814	- 2	0.5	-0.5	1

SYMM refers to symmetry operator: 1= X,Y,Z; 2= X,-Y,Z and TX, TY, TZ are unit cell translations.

In **D** there are two anions per cation, each with one ionized carboxyl group. For the carboxylate group, the mean of the C-O bond lengths is 1.261(6) Å. The dihedral angle between the carboxylic and carboxylate groups is 89°. These are inclined at 90 and 7.3° respectively from the least squares plane of the ring. The maximum deviation from the benzene ring is 0.0105 Å for C(1). The torsion angle H(11)-O(11)-C(11)-O(12) is -10°.

A plot of the crystal structure is shown in Figure 2. The structure is composed of sheets of cations parallel to the (1 0 0) plane separating double layers of anions. Anion-anion and anion-water hydrogen bonding (Table 4) leads to the formation of [anion-Mg.$2H_2O$-anion] 'sandwiches'. Anion-anion hydrogen bonds result in the formation of chains parallel to the *c* axis. Ionic Mg - O contacts also exist.

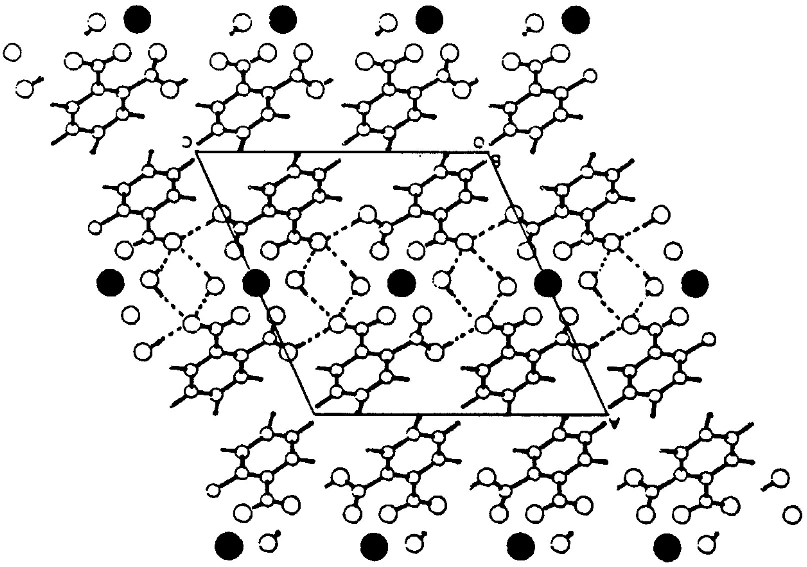


FIGURE 2 Crystal structure of **D** viewed along the b-axis. The broken lines represent hydrogen bond contacts.

The crystal packing of **D** is similar to that of di-aquomanganese hydrogen phthalate $[Mn(C_8H_5O_4)_2.2H_2O]^{16}$. (In the manganese structure, the mean cation - oxygen distance is 2.189 Å).

Structure of Hexa-aquomagnesium hydrogen phthalate (**H**)

The structure consists of magnesium cations, hydrogen phthalate anions and water molecules. Atomic fractional parameters are given in Table 2 and bond lengths and angles are presented in Table 3. The atom numbering for the anion is shown in Figure 3. The Mg^{2+} cations, which lie on centres of symmetry, are each coordinated to six molecules of water (Table 4). These form slightly distorted octahedra with a mean Mg - O distance of 2.069 (5) Å.

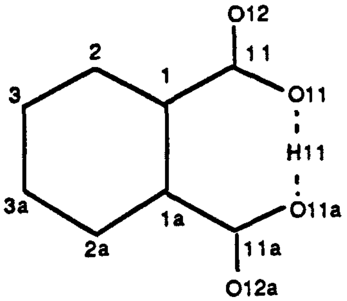


FIGURE 3. Anion atom numbering scheme for hexa-aquomagnesium hydrogen phthalate (**H**)

H(11), O(1) and O(2) are each located on a mirror plane whereas O(3) lies on a two-fold axis [O(1), O(2) and O(3) are the oxygens of water molecules]. The anion is almost planar, and for the ring atoms the maximum deviation from the least squares plane is 0.0039 Å (C(2)). The dihedral angle between the carboxyl group O(11)-C(11)-O(12) and the ring is 10.3°. A short intramolecular hydrogen bond is observed between the carboxyl groups of the anion. This bond is symmetrical as the anion lies on a mirror plane. A similar bond is found in lithium hydrogen phthalate dihydrate ($LiC_8H_5O_4.2H_2O$)[17], but is not symmetrical in this case.

The angle C(11)-C(1)-C(1a) is greater (128.4°) than those normally found in aromatic compounds. This results in a larger separation between the carboxyl groups.

Figure 4 is a plot of the crystal structure of **H** . In the structure the anions are held together by water-anion hydrogen bonds. The hydrogen bonding distances are shown in Table 4.

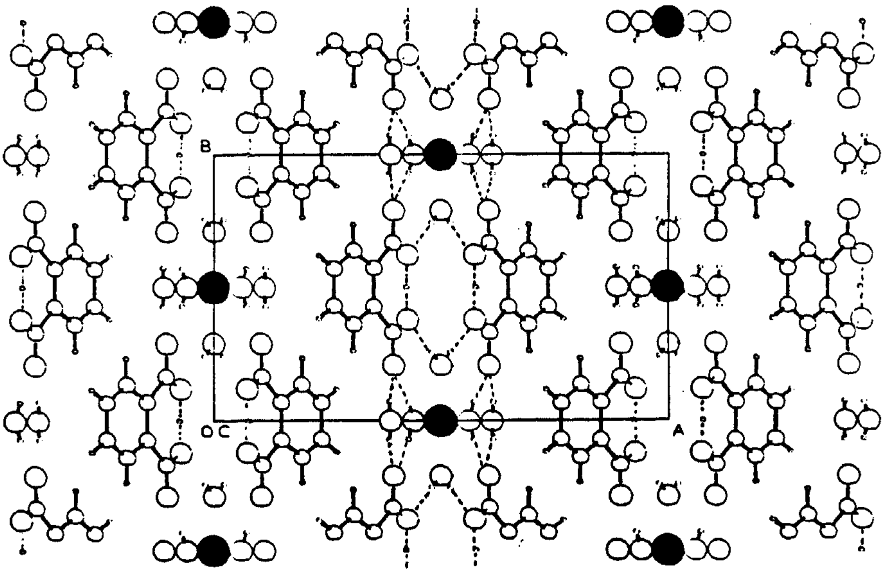


FIGURE 4. The crystal structure of **H** viewed down the c-axis. The broken lines indicate the hydrogen bond contacts.

The crystal structures of the cobolt derivative of C,[4] E[3] and F[3] have been reported elsewhere. Important crystallographic information for the various magnesium polymorphs are given in Table 5.

Thermal treatment of the different phases of magnesium hydrogen phthalate

Thermogravimetric analysis (TGA) gives an indication of the thermal stability of the various crystal structures. Heating C results in two weight losses - Figure 5(a) - commencing at approximately 60 °C (22%) and 140 °C (25%). For E two weight losses are observed (Figure 5(c)), commencing at about 90 (22%) and 150°C (28 %).

TABLE 5: Crystallographic data for the hydrogen phthalates including the cobolt analogue of C.

	COHPH	D	E	F	H
CRYSTAL SYSTEM	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
SPACE GROUP	$P2_1/a$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	C2/m
a(Å)	12.760(6)	12.916(1)	6.565(1)	7.042(1)	16.674(3)
b(Å)	5.319(4)	5.092(1)	30.840(4)	9.286(2)	9.811(2)
c(Å)	14.933(8)	12.956(2)	10.055(1)	9.549(2)	6.288(2)
α(°)	-	-	-	84.31(1)	-
β(°)	91.05(4)	113.98(1)	89.22(1)	109.34(1)	98.20(2)
γ(°)	-	-	-	108.99(1)	-
UNIT CELL VOLUME(Å^3)	1013.3	778.6	2035.5	557.1	1018.0
Z	2	2	4	1	2

The losses occurring below 140°C are attributed to the elimination of water of hydration and the magnitude of the weight losses are in agreement with the obtained crystal structures. (Both **C** and **E** contains six molecules of water per formula unit, which theoretically accounts for ~23% of their weight.)

In the case of **F** three drops in weight are recorded, these commencing at about 60 (6.4%), 80 (22%) and 140°C (27%). The structure of this phase reveals eight molecules of water and we assign the first two weight losses to the expulsion of two and then six water molecules, which theoretically account for ~7 and 22% of the total weight respectively. In the structure of **F**, two molecules of water per formula unit are not directly coordinated to the Mg^{2+} and are therefore easier to remove than the other structural water.

A single weight loss of about 42% was observed for **D** above 140°C. This result implies that in this material, the two molecules of water of hydration are held tightly until the entire structure is broken.

For **F**, **E** and **D**, the expulsion of water begins at 60, 90 and 140°C respectively. A similar trend is also observed in the temperatures at which the samples were obtained from aqueous solution. Thus **F** crystallizes at room temperature, and **E** and **D** at 50 and 80°C respectively. (**C** resulted from the solid state rehydration of an amorphous phase **B**).[4]

Above 140°C the observed changes are associated with the result of loss of at least part of the organic component of the salts. Long needle-like crystals (**I**) are formed on the colder parts of the apparatus when all the samples are heated above this temperature. Mass spectra for both these crystals and the amorphous residue (**J**) obtained by heating F showed peaks at m/e 76, 104 and 148 - assignable to C_6H_4, C_6H_4CO and $C_6H_4C(O)CO_2$ fragments. Absorption at 1853 and 1763 cm^{-1} in the infra-red spectrum of the crystals suggests the presence of the acid anhydride (-CO-O-CO-) group. For the residue, the absorptions at 1564 and 1419 cm^{-1} due to the carboxylate group occurred. No absorption was observed near 1700 cm^{-1}. The ^{13}C solution NMR results for these two materials revealed four chemical environments.

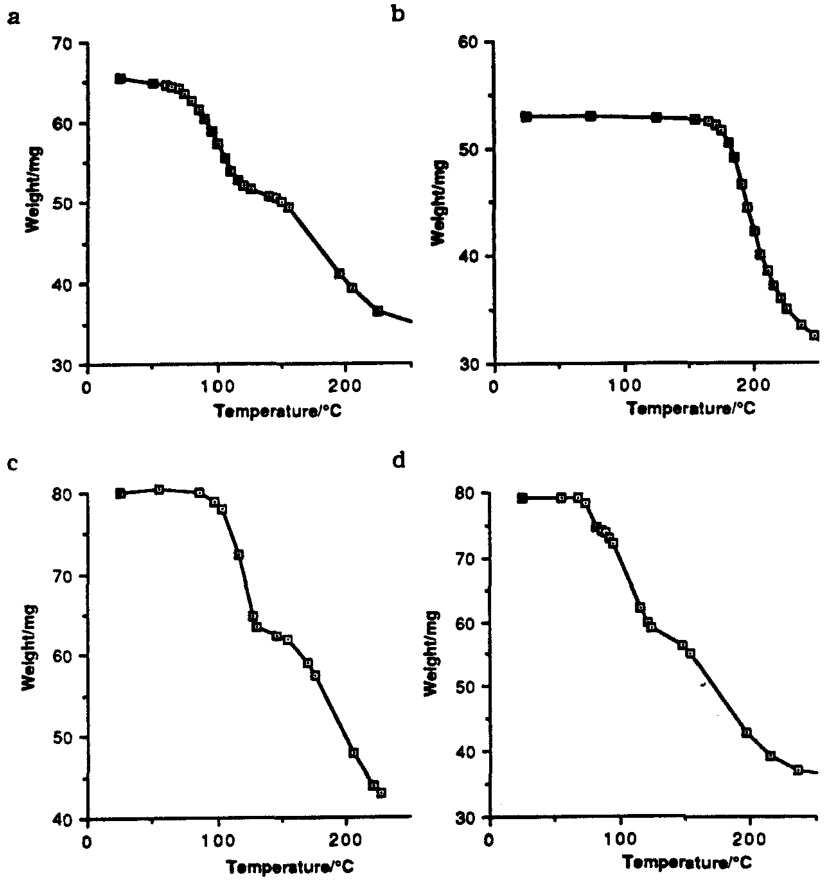


FIGURE 5: TGA plots showing weight losses below 300°C for: (a) C (22 and 25%), (b) D (42%), (c) E (22 and 28%) and (d) F (6.4, 22 and 27%).

These results show that the crystals (I) and residue (J) are phthalic anhydride and magnesium phthalate respectively. Microanalysis results (see Table 1 earlier) are are in agreement with this interpretation.

The transformation of F to H

The transformation of F to H involves dehydration:

$$Mg(H_2O)_6(C_8H_5O_4)_2.2H_2O \rightarrow Mg(H_2O)_6(C_8H_5O_4)_2 + 2H_2O$$

The loss of water of crystallization does not cause great disruption of the crystal structure and thus takes place in a single-crystal to single-crystal manner. A crystal suitable for data collection was obtained after the expulsion of the water molecules not coordinated to the magnesium ion. The structure was solved and refinement gave an R factor of 13.6%. The structure obtained was identical to that of **H**. Figure 6 is the experimental PXRD pattern for the sample obtained on dehydration of **F** in the TGA apparatus. The simulated pattern for **H** (Figure 6) is identical to that of the dehydration product.

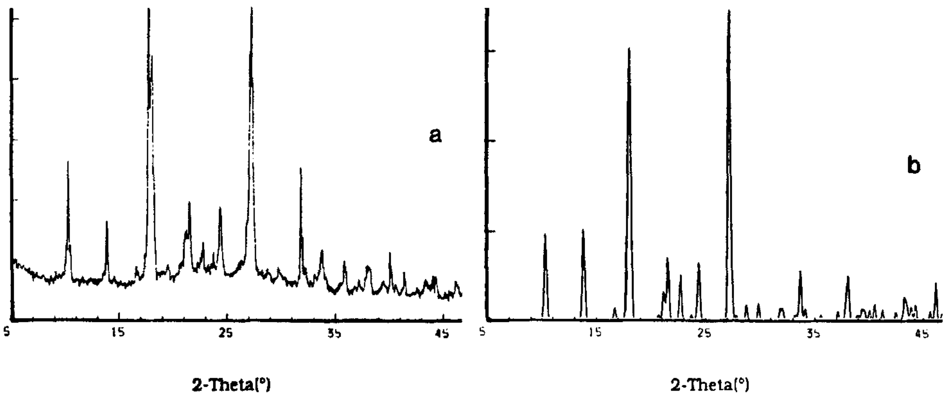


FIGURE 6. The (a) experimental and (b) simulated powder X-ray patterns for **H**.

DISCUSSION

General packing considerations in the hydrogen phthalates

In the magnesium hydrogen phthalate structures described here and elsewhere, the cations lie on centres of symmetry and each is surrounded by six oxygen atoms. These may all be from the water molecules or from both water and the anions. Incorporation of water takes place to different extents: **D** contains two; **C**, **E** and **H** have six; and **F** has eight molecules per formula unit.

The particular phase which crystallizes is found to depend on the solvent as well as the temperature. Thus **E** is obtained at room temperature (~22°C) from a saturated solution of **F** in methanol and at 50-80°C from water. When magnesium hydrogen phthalate is recrystallized from water at room temperature, **F** results. (The effect of the solvent on the mode of crystallization is also demonstrated by *p*-formylcinnamic acid[18]. Ethanol yields the photoreactive β form while the photostable γ form is obtained from acetone).

Another interesting observation is that a saturated solution of **E** in methanol resulted in **H** on standing at room temperature. Therefore at room temperature, solutions of **F** and **E** in methanol yield different phases; **E** and **H** respectively. A possible explanation could be that the form obtained depends on the amount of water present in the solution. (**F** contains a larger percentage (by ~6%) of water than **E**).

In the hydrogen phthalate structures, the C-O distances in the carboxylate groups are equivalent. Similar C-O distances and almost equivalent C-C-O angles are normally found in ionized carboxyl groups.[19] An unionized carboxyl displays two C-O distances, ~1.21 (C=O) and ~1.30 Å (C-OH). Two distinct C-C-O angles are also observed, ~113 (C-C-OH) and ~122 Å (C-C=O). Steric effects may also affect the bond angles. Thus for *o*-halogenobenzoic acids, the C-C=O angle increases with size of substituent.[20]

Conformational polymorphism, which is the occurrence of a compound in more than one crystal structure with different conformations, is observed. **C**, **E** and **H** have the same chemical formula $[Mg(H_2O)_6(C_8H_5O_4)_2]$, for example. The differences in the arrangement of the components and in the conformations of the anions are determined by the interactions which occur during nucleation as demonstrated by the solvent effects. Energy differences in such polymorphs are generally of the order of 2-3 kcal/mol.[21]

Two general modes of packing may be considered in these hydrogen phthalate structures; either in sandwich- or sheet-like arrangements.

Sandwich packing

In the structures of **C**, **D** and **E**, sandwich packing is observed with the following features:

1) Hydrogen bonding involving the carboxylic hydrogen of one and the carbonyl group of another link the anions together.

2) The carboxyl groups are turned towards the $Mg(H_2O)_x^{2+}$ as a result of hydrogen bonding between the water molecules and the anions (and Mg - O ionic contacts in **D**).

3) Thus [anion-(cation+H_2O)-anion] 'sandwiches' are formed. The interaction between the 'sandwiches' is through van der Waals interactions.

4) The dihedral angles between the ring and the carboxyl groups vary to allow the above to occur. For example, the dihedral angles the ring makes with the carboxylic and carboxylate groups are 7.0 and 71.8 respectively for **C** and 90.0 and 7.3 respectively for **D**.

These observations also apply to some other hydrogen phthalate structures- see Table 6 which also lists some structural information. The coordination refers to the number of oxygen atoms up to ~3 Å from the cation. With reference to point 2 above, direct interactions may occur between the cations and oxygen atoms of the anions, instead of anion-water hydrogen bonds.

TABLE 6 Structural details for hydrogen phthalates which display sandwich- and sheet-like packing.

(a) Sandwich packing

	cation coord.	Angle (°) between ring & carboxyl groups		reference
$KC_8H_5O_4$	6	75.4	31.7	19
$NaC_8H_5O_4.{}^1/_2H_2O$	6	67	27	22
$RbC_8H_5O_4$	6	71	32	23
$NH_4C_8H_5O_4$	6	74	26	24,25
$Sr(C_8H_5O_4)_2.2H_2O$	9	71	28	26
$Mn(C_8H_5O_4)_2.2H_2O$	6	5	88	16
$Co(C_8H_5O_4)_2.6H_2O$	6	69.6	28.7	27
		98.8	15.7	

(b) Sheetlike packing

$Cu(C_8H_5O_4)_2.2H_2O$	6	16.5	-19.0	28
$LiC_8H_5O_4.2H_2O$	4	0	0	17
$LiC_8H_5O_4.H_2O$	4	23.4	31.7	29
		20.7	16.6	
$LiC_8H_5O_4.CH_3OH$	4	21.2	-19.8	30
		24.9	-26.7	

The structure of $NH_4C_8H_5O_4.{}^1/_2H_2O$ is disordered[31] and the angles between the planes of the carboxyl groups and the ring are 7 and 85°.

Sheet packing

For **F** and **H** it is observed that:

1) A short intramolecular hydrogen bond exists. The O=C-O-H group is antiplanar.

2) The anions are essentially planar and they pack in a layerlike fashion.

3) There is no hydrogen bonding between the anions. The structures are held together by a network of hydrogen bonds between the anions and the water molecules.

These features are also found in other hydrogen phthalate structures- see Table 6. In addition to the mentioned contacts, direct anion-cation interaction also occur in these compounds.

CONCLUDING REMARKS

It is clear that a range of polymorphic forms are possible for the phthalate salts and that both temperature and the availability of water control which polymorph is obtained. Scheme 2 indicates that only one of these polymorphs is accessible by the solid state decomposition of the peroxy salt.[2]

Our studies[32] of other peroxy acid salts suggests that similar complex chemistry is available although to date the generation of amorphous intermediate phases is most common in the case of magnesium.

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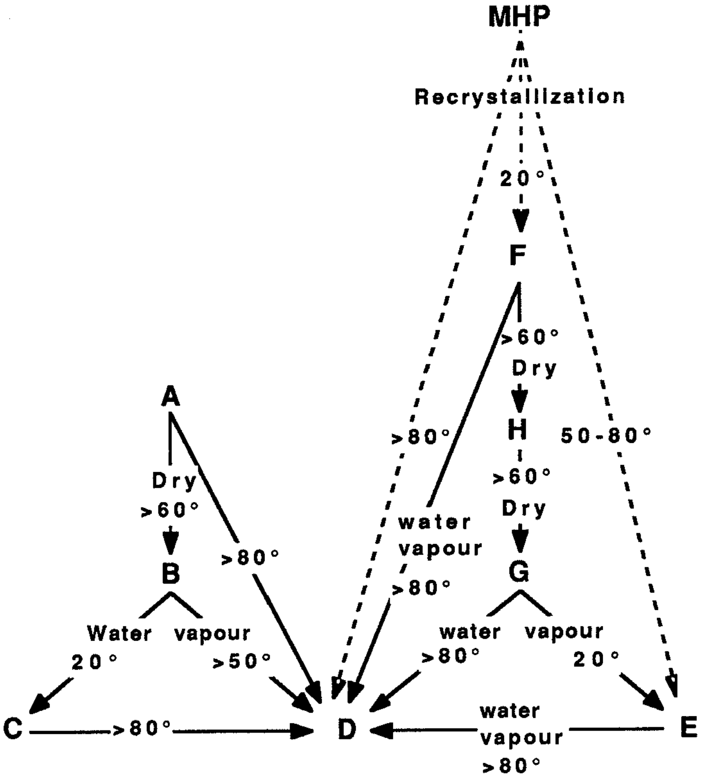

SCHEME 2

A - hexa-aquomagnesium monoperoxyphthalate

MHP - solution of magnesium hydrogen phthalate in water

B - H - solid forms of magnesium hydrogen phthalate

The temperatures given are approximate (°C).

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