Acta Cryst. (1989). C**45**, 1297–1299

Structures of Hexaaquamagnesium Hydrogen Phthalate and Hexaaquamagnesium Hydrogen Phthalate Dihydrate

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(*Received* 18 *January* 1989; *accepted* 25 *April* 1989)

Abstract. (I): $[Mg(H_2O)_6](C_8H_5O_4)_2$, $M_r = 462{\cdot}65$, monoclinic, $P2_1/c$, $a = 6{\cdot}565(1)$, $b = 30{\cdot}840(4)$, $c = 10{\cdot}055(1)$ Å, $\beta = 89{\cdot}22(1)^\circ$, $V = 2035{\cdot}5$ Å^3, $Z = 4$, $D_x = 1{\cdot}51$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}13$ cm^{-1}, $F(000) = 960$, $T = 295$ K, $R = 0{\cdot}069$ for 1259 observed reflections. (II): $[Mg(H_2O)_6](C_8H_5O_4)_2.2H_2O$, $M_r = 498{\cdot}68$, triclinic, $P\bar{1}$, $a = 7{\cdot}0418(8)$, $b = 9{\cdot}2859(13)$, $c = 9{\cdot}5492(14)$ Å, $\alpha = 84{\cdot}31(1)$, $\beta = 109{\cdot}34(1)$, $\gamma = 108{\cdot}99(1)^\circ$, $V = 557{\cdot}1$ Å^3, $Z = 1$, $D_x = 1{\cdot}49$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}12$ cm^{-1}, $F(000) = 260$, $T = 295$ K, $R = 0{\cdot}098$ for 942 observed reflections. The Mg^{2+} cation is octahedrally coordinated to water molecules with mean Mg—O distances of 2·081(9) Å in both structures. In the anhydrous form the structure is made up of sheets of cations separating double layers of anions. In the hydrated structure, both cations and anions form columns along the *a* axis. In both structures there is an extensive hydrogen-bonding network with the hydrated form containing, in addition, a short intramolecular contact of 2·384(14) Å between the O atoms of two carboxylic groups.

Introduction. The crystal structures of the title compounds have been determined in connection with studies of thermal solid-state reactions of some derivatives of phthalic acid. Our interest stems in part from an investigation of substituent effects in crystal engineering (Theocharis & Jones, 1987) as well as an analysis of the role of water as a mediator in solid-state reactions (Wang, Kariuki & Jones, 1989).

Experimental. For (I): white transparent crystals, 0·2 × 0·1 × 0·2 mm, were obtained at 358 K. Lattice parameters were refined using 25 reflections in the range $9 \le \theta \le 15^\circ$. 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 1259 observed X-ray intensities ($F > 3\sigma F$) were recorded in the range $1{\cdot}5 \le \theta \le 25^\circ$ (index range h −7/7, k 0/36, l 0/11). Standard reflections $1\bar{9}3$, $\bar{1},\overline{13},3$, $\bar{2},\overline{11},0$ were recentred every 100 reflections and scanned every 3 h to check for movement and stability of the crystal. No significant deviation was observed. The structure was solved by direct methods using *SHELXS*84 (Sheldrick, 1984) and refined (on F) by blocked full-matrix least-squares analysis using *SHELX*76 (Sheldrick, 1976). All H atoms, except those on the water molecules and one carboxylic group [H(211) in Fig. 1(*a*)], were located in the difference Fourier synthesis map. Isotropic refinement resulted in very low thermal parameters for some H atoms. All non-H atoms were assigned anisotropic thermal parameters to give an R value of 0·069. No absorption correction or weighting was applied. In the final cycle of refinement maximum shift/e.s.d. was 0·317. Final maximum and minimum heights in final difference Fourier synthesis map were 0·43 and −0·37 e Å^{-3}, respectively.

For (II): white transparent crystals, 0·1 × 0·1 × 0·2 mm, were obtained by reacting stoichiometric amounts of magnesium oxide and phthalic acid in water and allowing slow evaporation. Optical and X-ray photography showed that the crystal used in this determination was twinned. A better one could not be obtained but no difficulties were experienced in the structure determination and refinement. The twinning may, however, account for the relatively high R value. Experimental details as for (I). A total of 942 observed X-ray intensities ($F > 3\sigma F$) were recorded in the range $1{\cdot}5 \le \theta \le 30^\circ$ (index range h −9/9, k −13/13, l 0/13). Standard reflections $\bar{4}33$, 050, 040 were recentred every 100 reflections and $2\bar{1}3$, $\bar{4}32$, 040 were scanned every 3 h to check for movement and stability of the crystal; no significant deviation was observed. Structure solution and refinement as for (I). The H atom of the carboxylic group was located in the difference Fourier synthesis map. All non-H atoms were assigned anisotropic thermal parameters and ring H atoms were fixed geometrically to give a final R value of 0·098. No absorption correction or weighting was applied and the water H atoms were not located. In the final cycle of refinement maximum shift/e.s.d. was 0·129. Final maximum and minimum heights in the difference Fourier synthesis were 0·63 and −0·62 e Å^{-3}, respectively. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974) were used throughout.

0108-2701/89/091297-03\$03.00

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* (Å²) *for non*-H *atoms with e.s.d.'s in parentheses*

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}
(*a*) Compound (I)				
Mg(1)	0·5000	0·5000	0·5000	0·0250
Mg(2)	0·0000	0·5000	0·0000	0·0316
O(1)	0·6589 (10)	0·0330 (2)	0·8447 (7)	0·0299
O(2)	0·4771 (11)	0·0564 (2)	1·1037 (7)	0·0377
O(3)	0·2269 (11)	0·0118 (2)	0·9050 (7)	0·0348
O(4)	−0·1604 (15)	0·5247 (3)	0·1613 (9)	0·0591
O(5)	1·0306 (11)	0·4431 (2)	1·1055 (7)	0·0363
O(6)	1·2749 (14)	0·5248 (3)	1·0789 (10)	0·0665
C(11)	0·2809 (16)	0·3328 (3)	0·0118 (11)	0·0276
C(12)	0·3866 (15)	0·3484 (4)	0·1190 (11)	0·0303
C(13)	0·3838 (17)	0·3249 (4)	0·2375 (11)	0·0404
C(14)	0·2865 (18)	0·2856 (4)	0·2458 (13)	0·0430
C(15)	0·1838 (18)	0·2697 (4)	0·1391 (13)	0·0434
C(16)	0·1752 (16)	0·2942 (4)	0·0252 (12)	0·0349
C(111)	0·2773 (15)	0·3571 (3)	−0·1143 (10)	0·0266
C(121)	0·5132 (16)	0·3906 (3)	0·1175 (9)	0·0282
O(111)	0·2147 (11)	0·3356 (2)	−0·2184 (7)	0·0356
O(112)	0·3318 (12)	0·3957 (2)	−0·1202 (7)	0·0414
O(121)	0·4310 (12)	0·4232 (2)	0·1713 (9)	0·0480
O(122)	0·6896 (11)	0·3879 (3)	0·0719 (8)	0·0398
C(21)	0·2235 (15)	0·6645 (3)	0·3636 (10)	0·0259
C(22)	0·1217 (14)	0·6496 (3)	0·4792 (11)	0·0246
C(23)	0·1244 (17)	0·6738 (4)	0·5917 (12)	0·0376
C(24)	0·2229 (19)	0·7133 (4)	0·5939 (13)	0·0482
C(25)	0·3199 (19)	0·7283 (4)	0·4836 (14)	0·0430
C(26)	0·3289 (17)	0·7037 (4)	0·3696 (12)	0·0346
C(211)	0·2327 (17)	0·6373 (3)	0·2400 (12)	0·0324
C(221)	−0·0125 (16)	0·6099 (3)	0·4789 (10)	0·0290
O(211)	0·2531 (11)	0·6596 (2)	0·1297 (7)	0·0385
O(212)	0·2180 (12)	0·5980 (2)	0·2430 (8)	0·0384
O(221)	0·0271 (11)	0·5784 (3)	0·5544 (8)	0·0427
O(222)	−0·1730 (11)	0·6117 (3)	0·4097 (7)	0·0406
(*b*) Compound (II)				
Mg	0·0000	0·5000	0·0000	0·0297
O(1)	0·8937 (13)	0·2653 (9)	0·9955 (9)	0·0301
O(2)	0·7766 (14)	0·5017 (10)	0·7953 (9)	0·0367
O(3)	0·2273 (14)	0·4992 (10)	0·9003 (9)	0·0401
O(4)	0·3941 (15)	0·2553 (11)	0·9990 (9)	0·0457
C(1)	0·2885 (18)	−0·0068 (13)	0·5726 (11)	0·0215
C(2)	0·1946 (20)	−0·0091 (14)	0·4145 (13)	0·0297
C(3)	0·0587 (21)	−0·1478 (13)	0·3477 (13)	0·0332
C(4)	0·0091 (21)	−0·2780 (14)	0·4268 (15)	0·0375
C(5)	0·0989 (23)	−0·2765 (16)	0·5792 (15)	0·0423
C(6)	0·2354 (21)	−0·1420 (14)	0·6492 (13)	0·0351
C(11)	0·4432 (22)	0·1269 (15)	0·6738 (15)	0·0379
C(21)	0·2280 (21)	0·1222 (15)	0·3098 (14)	0·0376
O(11)	0·5020 (17)	0·2589 (12)	0·6186 (11)	0·0478
O(12)	0·5048 (15)	0·1082 (11)	0·8088 (9)	0·0456
O(21)	0·1351 (16)	0·0944 (11)	0·1735 (10)	0·0471
O(22)	0·3441 (15)	0·2540 (10)	0·3556 (9)	0·0419

Table 2. *Magnesium environment, bond distances* (Å) *and bond angles* (°)

(*a*) Compound (I)			
O(2)—Mg(1)	2·032 (9)	O(3)—Mg(1)	2·074(9)
O(1)—Mg(1)	2·125 (9)	O(4)—Mg(2)	2·067 (9)
O(5)—Mg(2)	2·061 (7)	O(6)—Mg(2)	2·124 (9)
O(1)—Mg(1)—O(2)	90 (4)	O(1)—Mg(1)—O(3)	89·8 (4)
O(2)—Mg(1)—O(3)	91·6 (4)	O(4)—Mg(2)—O(5)	87·8 (3)
O(4)—Mg(2)—O(6)	90·0 (4)	O(5)—Mg(2)—O(6)	91·4 (3)
C(11)—C(12)	1·376 (15)	C(11)—C(16)	1·384 (16)
C(11)—C(111)	1·473 (15)	C(12)—C(13)	1·396 (16)
C(13)—C(14)	1·372 (18)	C(15)—C(14)	1·366 (18)
C(15)—C(16)	1·376 (18)	C(111)—O(112)	1·242 (13)
C(111)—O(111)	1·310 (12)	C(121)—C(12)	1·544 (15)
C(121)—O(122)	1·242 (13)	C(121)—O(121)	1·259 (13)
C(26)—C(21)	1·395 (15)	C(26)—C(25)	1·377 (18)
C(211)—C(21)	1·500 (15)	C(211)—O(211)	1·311 (14)
C(22)—C(23)	1·356 (16)	C(22)—C(21)	1·409 (15)
C(211)—O(212)	1·214 (13)	C(23)—C(24)	1·378 (18)
C(24)—C(25)	1·354 (19)	C(221)—C(22)	1·508 (14)
C(221)—O(222)	1·271 (13)	C(221)—O(221)	1·263 (13)
C(14)—C(15)—C(16)	118·8 (11)	C(12)—C(121)—O(122)	116·5 (9)
C(12)—C(121)—O(121)	116·1 (9)	O(122)—C(121)—O(121)	127·1 (10)
C(12)—C(11)—C(111)	120·7 (10)	C(12)—C(11)—C(16)	118·8 (10)
C(111)—C(11)—C(16)	120·5 (10)	C(121)—C(12)—C(11)	124·3 (10)
C(121)—C(12)—C(13)	116·6 (9)	C(11)—C(12)—C(13)	119·1 (10)
C(12)—C(13)—C(14)	120·8 (11)	C(15)—C(14)—C(13)	120·3 (12)
C(11)—C(111)—O(111)	116·0 (9)	C(11)—C(111)—O(112)	121·3 (9)
C(15)—C(16)—C(11)	121·9 (11)	O(111)—C(11)—O(112)	122·7 (9)
C(26)—C(21)—C(22)	118·5 (10)	C(26)—C(21)—C(211)	120·4 (9)
C(22)—C(21)—C(211)	121·0 (9)	C(23)—C(24)—C(25)	120·4 (12)
C(26)—C(25)—C(24)	120·5 (11)	C(22)—C(221)—O(222)	117·0 (9)
C(22)—C(221)—O(221)	119·9 (9)	O(222)—C(221)—O(221)	122·8 (10)
C(21)—C(26)—C(25)	119·9 (11)	C(221)—C(22)—C(23)	117·6 (9)
C(221)—C(22)—C(21)	122·2 (9)	C(23)—C(22)—C(21)	119·8 (10)
C(21)—C(211)—O(211)	114·2 (9)	C(21)—C(211)—O)212)	122·3 (10)
C(22)—C(23)—C(24)	120·7 (11)	O(211)—C(211)—O(212)	123·5 (10)
(*b*) Compound (II)			
O(1)—Mg	2·061 (7)	O(1)—Mg—O(3)	90·2 (3)
O(2)—Mg	2·066 (8)	O(2)—Mg—O(3)	91·7 (3)
O(3)—Mg	2·117 (10)	O(1)—Mg—O(2)	89·6 (3)
C(1)—C(6)	1·394 (15)	C(1)—C(2)	1·432 (15)
C(1)—C(11)	1·524 (16)	C(2)—C(3)	1·392 (16)
C(2)—C(21)	1·506 (16)	C(3)—C(4)	1·368 (17)
C(5)—C(6)	1·374 (17)	C(5)—C(4)	1·380 (18)
C(11)—O(11)	1·279 (16)	C(11)—O(12)	1·229 (15)
C(21)—O(22)	1·255 (14)	C(21)—O(21)	1·257 (14)
C(6)—C(1)—C(2)	118·2 (10)	C(6)—C(1)—C(11)	113·2 (10)
C(2)—C(1)—C(11)	128·6 (10)	C(3)—C(2)—C(1)	117·3 (10)
C(3)—C(2)—C(21)	115·3 (10)	C(1)—C(2)—C(21)	127·4 (10)
C(2)—C(3)—C(4)	122·8 (12)	C(3)—C(4)—C(5)	120·1 (12)
C(6)—C(5)—C(4)	118·8 (8)	C(1)—C(6)—C(5)	122·7 (11)
O(12)—C(11)—C(1)	119·6 (11)	O(11)—C(11)—O(12)	120·5 (11)
C(1)—C(11)—O(11)	119·9 (11)	O(22)—C(21)—O(21)	121·0 (12)
O(22)—C(21)—C(2)	121·8 (11)	O(21)—C(21)—C(2)	117·2 (11)

Discussion. Atomic fractional parameters for both structures are given in Table 1.* Bond lengths and angles are given in Table 2. The atom numbering is shown in Figs. 1(*a*) and 1(*b*) for the anhydrous and hydrated forms respectively.

$[Mg(H_2O)_6](C_8H_5O_4)_2$ (I). The Mg^{2+} ions occupy two independent special positions in the asymmetric unit and are surrounded by six water molecules (Table 2*a*). There are two anion molecules in the asymmetric unit, each with one ionized COOH group. Bond distances and angles are not significantly different from those observed in $Sr(C_8H_5O_4)_2.2H_2O$ (Bats, Schuckmann & Fuess, 1978), $KC_8H_5O_4$ (Okaya, 1965), $NaC_8H_5O_4.0{\cdot}5H_2O$ (Smith, 1975*a*), $[NH_4]C_8H_5O_4$ (Smith, 1975*c*; Okaya & Pepinsky, 1957), $RbC_8H_5O_4$ (Smith, 1975*b*) and $[NH_4]C_8H_5O_4.0{\cdot}5H_2O$ (Smith, 1977). In the anion, interplanar angles between the —CO_2 groups and benzene rings range from 15 to 83°. A *PLUTO* plot (Motherwell & Clegg, 1978) of the crystal structure is shown in Fig. 2. The structure is made up of sheets of cations separating double layers of anions. A network of hydrogen bonds exists between the water molecules and O atoms of the two nearest layers of

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*Structure-factor listings, anisotropic thermal parameters, H-atom positions and complete molecular geometry listings (including hydrogen-bond details) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51840 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

anions. Intermolecular O–O distances range from 2·526(11) to 3·329(11) Å.

$[Mg(H_2O)_6](C_8H_5O_4)_2.2H_2O$ (II). The Mg^{2+} ion occupies a centre of symmetry and is surrounded by six water molecules (Table 2*b*). The anion is planar except for the carboxylic H. The plane through C(1) to C(6) can be represented by the equation $0{\cdot}7693x - 0{\cdot}4886y - 0{\cdot}4116z = -0{\cdot}2494$ with deviations less than 0·008 Å. The deviations of O(22), O(12), O(21), O(11), C(21), C(11) and H(11) from this plane are −0·0414, −0·0118, 0·0281, −0·0208, −0·0094, 0·0067 and −0·2234 Å respectively. One COOH group is ionized. A *PLUTO* plot (Motherwell & Clegg, 1978) of the crystal structure is shown in Fig. 3. The ions pack in columns along the *a* axis. Extensive hydrogen bonding exists in the crystal with intermolecular O–O distances in the range 2·725(14) to 3·002(14) Å. A short intramolecular hydrogen bond with a distance of 2·384(14) Å between the O atoms of two carboxylic groups is observed. Similar intramolecular bonds exist in $Cu(C_8H_5O_4)_2.2H_2O$ (Cingi, Guastini, Musati & Nardelli, 1969), $LiC_8H_5O_4.2H_2O$ (Gonschorek & Küppers, 1975), $LiC_8H_5O_4.CH_3OH$ (Adiwidjaja & Küppers, 1978) and $LiC_8H_5O_4.H_2O$ (Küppers, 1978).

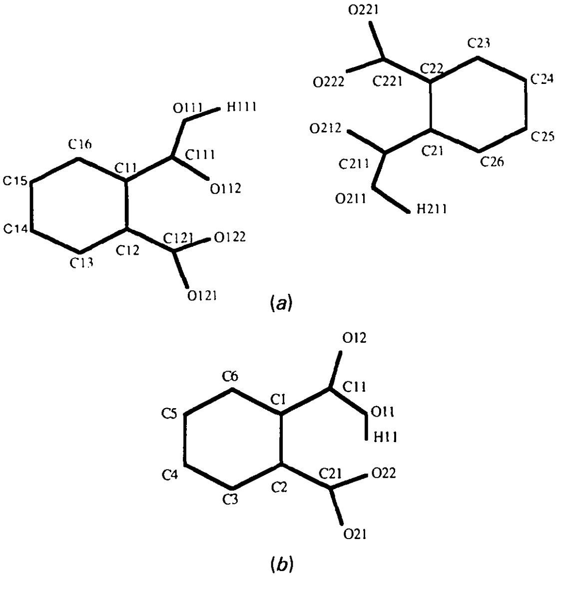

Fig. 1. Anion atom numbering for (*a*) the anhydrous and (*b*) the hydrated form of hexaaquamagnesium hydrogen phthalate.

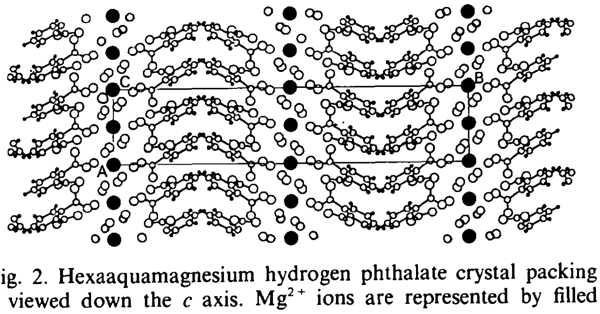

Fig. 2. Hexaaquamagnesium hydrogen phthalate crystal packing viewed down the *c* axis. Mg^{2+} ions are represented by filled circles.

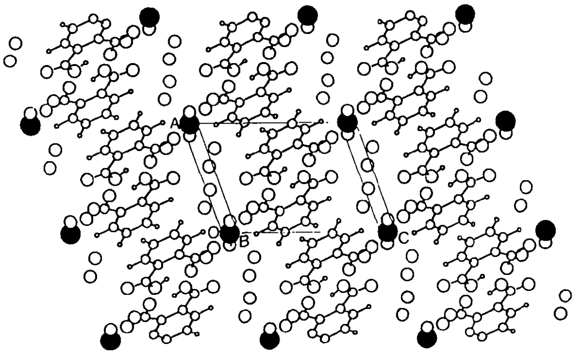

Fig. 3. Hexaaquamagnesium hydrogen phthalate dihydrate crystal packing viewed down the *b* axis. Mg^{2+} ions are represented by filled circles.

Support of the Cambridge Commonwealth Trust (Studentship for BMK) and Interox Ltd is appreciated.

References

Adiwidjaja, G. & Küppers, H. (1978). *Acta Cryst.* **B34**, 2003–2005.

Bats, J.W., Schuckmann, W. & Fuess, H. (1978). *Acta Cryst.* **B34**, 2627–2628.

Cingi, M. B., Guastini, C., Musati, A. & Nardelli, M. (1969). *Acta Cryst.* **B25**, 1833–1840.

Gonschorek, W. & Küppers, H. (1975). *Acta Cryst.* **B31**, 1068–1072.

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

Küppers, H. (1978). *Acta Cryst.* **B34**, 3763–3765.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Okaya, Y. (1965). *Acta Cryst.* **19**, 879–882.

Okaya, Y. & Pepinsky, R. (1957). *Acta Cryst.* **10**, 324–328.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1984). *SHELXS84*. Program for crystal structure solution. Univ. of Göttingen, Federal Republic of Germany.

Smith, R. A. (1975*a*). *Acta Cryst.* **B31**, 2345–2347.

Smith, R. A. (1975*b*). *Acta Cryst.* **B31**, 2347–2348.

Smith, R. A. (1975*c*). *Acta Cryst.* **B31**, 2508–2509.

Smith, R. A. (1977). *Acta Cryst.* **B33**, 1594–1596.

Theocharis, C. R. & Jones, W. (1987). *Organic Solid State Chemistry*, edited by G. R. Desiraju, pp. 47–67. Amsterdam: Elsevier.

Wang, W-N., Kariuki, B. M. & Jones, W. (1989). In preparation.