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Refinement of the Structure of Calcium Phthalate Monohydrate

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Abstract. $Ca(C_8H_4O_4).H_2O$, monoclinic, $P2_1/c$, $Z = 4$, $a = 11{\cdot}213$ (8), $b = 6{\cdot}680$ (5), $c = 11{\cdot}988$ (8) Å, $\beta = 98{\cdot}91$ (5)°, $V = 887$ Å^3, $D_c = 1{\cdot}68$ g cm^{-3}; single-crystal diffractometer data up to $\sin\theta/\lambda = 0{\cdot}70$ Å^{-1}; Mo $K\alpha$ radiation, Nb-filtered. The structure was refined to $R = 0{\cdot}029$ for 2451 reflections. All H atoms were located. The water molecule is linked by two hydrogen bonds to the carboxyl groups. The results are compared with those of earlier work. The hydrogen-bond system reported previously was found to be in error.

Introduction. Calcium phthalate was obtained by the reaction of an excess of phthalic acid with $CaCO_3$ in boiling water. Colourless crystals were formed on cooling. Cell dimensions and the space group were derived from precession photographs. The cell dimensions refined from diffractometer data are slightly different from those reported earlier (Cingi, 1959; Gupta & Sinha, 1975, hereafter GS). Intensities were measured on a computer-controlled four-circle Hilger & Watts diffractometer with Nb-filtered Mo $K\alpha$ radiation and the $\theta/2\theta$ scan technique. 2593 unique reflections with $\sin\theta/\lambda < 0{\cdot}70$ Å^{-1} were obtained from a crystal 0·3 × 0·2 × 0·2 mm. 2451 reflections had $I > 2\sigma(I)$ and were used for the refinement. The form factors for Ca^{2+}, C and O were taken from Cromer & Mann (1968), those for H from Stewart, Davidson & Simpson (1965). An anomalous-dispersion correction ($f' = 0{\cdot}2$, $f'' = 0{\cdot}3$) was applied to Ca. The heavy atoms were refined anisotropically. H atoms were located from difference maps and refined isotropically. An extinction parameter was introduced in the later stages. The final $R = 0{\cdot}029$ for the 2451 reflections and $R_w(F) = 0{\cdot}037$.

All calculations were carried out with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) on the Univac 1108 computer of the Hochschulrechenzentrum der Universität Frankfurt. The atomic parameters are listed in Table 1, bond distances and angles in Tables 2 and 3. The phthalate ion is shown in Fig. 1, and the packing in Fig. 2.†

Table 1. *Fractional atomic coodinates and their e.s.d.'s*

	x	y	z
C(1)	0·2871 (1)	0·2860 (2)	0·0718 (1)
C(2)	0·4010 (1)	0·3058 (2)	0·0404 (1)
C(3)	0·4956 (1)	0·1854 (2)	0·0895 (1)
C(4)	0·4772 (1)	0·0430 (2)	0·1685 (1)
C(5)	0·3635 (1)	0·0178 (2)	0·1978 (1)
C(6)	0·2685 (1)	0·1405 (2)	0·1506 (1)
C(7)	0·1827 (1)	0·4061 (2)	0·0122 (1)
C(8)	0·1477 (1)	0·1196 (1)	0·1869 (1)
O(1)	0·1705 (1)	0·5851 (1)	0·0412 (1)
O(2)	0·1154 (1)	0·3149 (1)	−0·0639 (1)
O(3)	0·1122 (1)	−0·0487 (1)	0·2149 (1)
O(4)	0·0847 (1)	0·2747 (1)	0·1918 (1)
O(5)	0·1765 (1)	0·5884 (2)	0·3763 (1)
Ca	0·0577 (1)	0·6195 (1)	0·1939 (1)
H(1)	0·413 (2)	0·396 (3)	−0·022 (2)
H(2)	0·572 (2)	0·203 (3)	0·065 (2)
H(3)	0·544 (2)	−0·037 (3)	0·204 (2)
H(4)	0·354 (2)	−0·086 (3)	0·256 (2)
H(5)	0·169 (2)	0·476 (4)	0·400 (2)
H(6)	0·174 (2)	0·674 (4)	0·418 (2)

Table 2. *Bond distances* (Å) *and angles* (°) *in the phthalate group*

C(1)–C(2)	1·393 (2)	C(6)–C(8)	1·492 (2)
C(1)–C(6)	1·393 (2)	C(7)–O(1)	1·259 (2)
C(2)–C(3)	1·387 (2)	C(7)–O(2)	1·249 (1)
C(4)–C(3)	1·380 (2)	C(8)–O(3)	1·256 (2)
C(4)–C(5)	1·384 (2)	C(8)–O(4)	1·261 (2)
C(5)–C(6)	1·393 (2)	O(5)–H(5)	0·81 (3)
C(1)–C(7)	1·505 (2)	O(5)–H(6)	0·76 (2)
C(2)–C(1)–C(7)	120·0 (1)	C(6)–C(8)–O(3)	120·1 (1)
C(6)–C(1)–C(7)	120·5 (1)	C(6)–C(8)–O(4)	118·5 (1)
C(1)–C(6)–C(8)	120·0 (1)	O(1)–C(7)–O(2)	125·9 (1)
C(5)–C(6)–C(8)	119·9 (1)	O(3)–C(8)–O(4)	121·3 (1)
C(1)–C(7)–O(1)	119·0 (1)	H(5)–O(5)–H(6)	116 (3)
C(1)–C(7)–O(2)	115·1 (1)		

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† Lists of structure factors and anisotropic thermal parameters (including the values given by GS) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33846 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The refinement of $Ca(C_8H_4O_4).H_2O$ is part of a study of the structure and bonding in salts of phthalic acid (Bats, Kallel & Fuess, 1978). The structure of the title compound was first reported by GS. Their refinement was carried out on 913 reflections from Weissenberg photographs. The present refinement is an order of magnitude more accurate. Comparison of the positions of the non-hydrogen atoms in the two studies shows them to agree within the 3σ limit. The differences are more pronounced for the anisotropic thermal parameters.* Fig. 3 shows normal probability plots for a comparison between (*a*) the positional, and (*b*) the anisotropic thermal parameters of GS and the present study. The slope of the distribution of the positional parameters is near to one but the mean value is different from zero. The anisotropic temperature parameters, however, show more pronounced deviations. u_{11} and u_{22} of the present study have systematically higher values than those reported by GS; this is reflected in the deviation of the mean from zero and the slope in the normal probability distribution. The normal probability distribution between observed and calculated structure factors of our data set showed a mean value of zero and a slope of one. The present study did not confirm the H atom positions of the water molecule reported by GS, resulting in a different hydrogen-bond system. The bond lengths given by GS for the phenyl ring vary between 1·35 (2) and 1·44 (2) Å, while the present work shows distances between 1·380 (2) and 1·393 (2) Å. The average C–H distance is 0·98 Å in our refinement. The O(3)–C(8)–O(4) angle of 121·3° is unusually small for a carboxyl group. Smaller angles (119·4–119·7°) have been found only in lithium hydrogen phthalate (Gonschorek & Küppers, 1975) where they can be explained by the occurrence of a short intermolecular hydrogen bond. The difference in O–C–O angles in the present compound is most likely due to different involvement of the carboxyl groups in Ca–O bonding. O(3) and O(4) show the shortest distances to the Ca^{2+} ion.

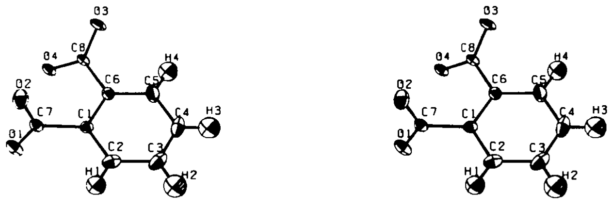

Fig. 1. Stereoscopic view of the phthalate group. The thermal ellipsoids are the 50% probability surfaces.

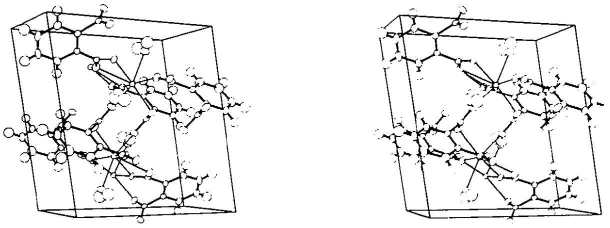

Fig. 2. Stereoscopic view of the packing.

Ca is surrounded by seven O atoms (Table 3) (six from phthalate ions, one from the water molecule) and it links the phthalate groups into infinite chains along **b**.

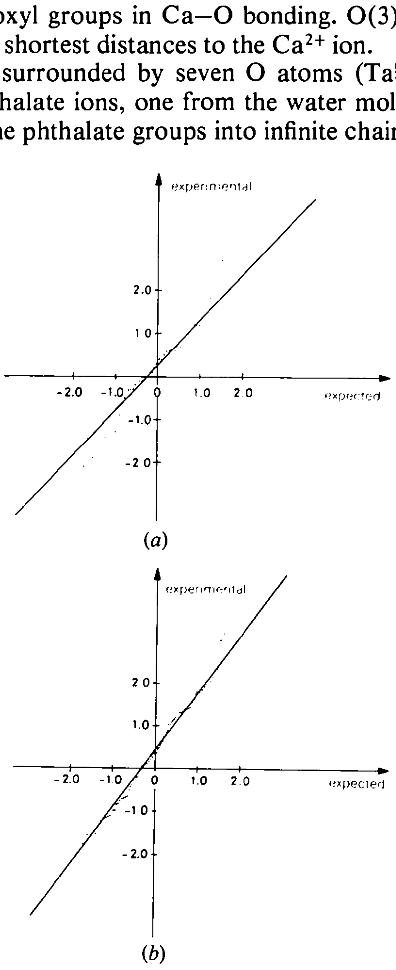

Fig. 3. Normal probability distribution (comparing GS and the present study) for (*a*) the positional parameters of the heavy atoms, and (*b*) the anisotropic temperature factors (*International Tables for X-ray Crystallography*, 1974).

Table 3. *Bond distances* (Å) *and angles* (°) *around* Ca^{2+}

Ca–O(1)	2·392 (2)	Ca–O(2)″	2·335 (2)
Ca–O(3)′	2·303 (2)	Ca–O(3)‴	2·595 (2)
Ca–O(4)	2·323 (2)	Ca–O(4)‴	2·486 (1)
Ca–O(5)	2·387 (2)		
O(1)–Ca–O(4)	79·1 (3)	O(5)–Ca–O(3)′	83·2 (4)
O(1)–Ca–O(5)	114·0 (6)	O(5)–Ca–O(4)‴	81·2 (6)
O(1)–Ca–O(2)″	89·4 (6)	O(3)′–Ca–O(4)‴	73·8 (4)
O(1)–Ca–O(3)′	90·8 (4)	O(3)′–Ca–O(2)″	94·1 (4)
O(4)–Ca–O(2)″	106·0 (3)	O(5)–Ca–O(3)‴	85·4 (6)
O(4)–Ca–O(3)‴	71·4 (4)	O(2)″–Ca–O(4)‴	75·6 (6)
O(4)–Ca–O(4)‴	121·0 (3)	O(3)‴–Ca–O(4)‴	51·1 (5)
O(4)–Ca–O(5)	82·5 (3)		

Atoms in equivalent positions are (′) $x, y+1, z$; (″) $\bar{x}, \bar{y}+1, \bar{z}$; (‴) $\bar{x}, y+\frac{1}{2}, \bar{z}+\frac{1}{2}$.

Table 4. *Hydrogen bonds*

O–H···O	O···O	H···O	∠O–H–O
O(5)–H(5)···O(2)	2·897 (2) Å	2·10 (3) Å	168°
O(5)–H(6)···O(1)	2·951 (2)	2·19 (3)	178

Table 5. *Deviations from best planes* (Å)

*P*1		*P*2		*P*3	
C(1)	0·008	C(1)	0·000	C(6)	0·003
C(2)	−0·010	C(7)	−0·001	C(8)	−0·011
C(3)	−0·001	O(1)	0·001	O(3)	0·004
C(4)	0·010	O(2)	0·001	O(4)	0·004
C(5)	−0·012				
C(6)	0·003				
C(7)	−0·108*				
C(8)	0·049*				
H(1)	−0·103*				
H(2)	−0·013*				
H(3)	0·037*				
H(4)	−0·024*				

Angles between planes (°)	
*P*1–*P*2	78
*P*1–*P*3	34
*P*2–*P*3	67

* Atoms not included in the calculation of the plane.

The structure has two hydrogen bonds (Table 4). Both involve the carboxyl group with the more normal O–C–O angle of 125·9°. They can be classified as rather weak. This system is described by GS as a bifurcated hydrogen-bond system where the same H atom of water is involved in both bonds. Our results indicate, however, a participation of both water H atoms in the two bonds. The maximum deviation of the atoms from the plane of the phenyl ring is 0·01 Å. Both carboxyl groups are planar (Table 5); their planes make angles of 78 and 34° with the phenyl ring and the angle between them is 67°.

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Polymeric 1,10-Phenanthrolinebis(phosphinato)manganese(II)

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Abstract. $C_{12}H_{12}MnN_2O_4P_2$, $P2_1/c$, $a = 10{\cdot}791\ (9)$, $b = 11{\cdot}173\ (8)$, $c = 13{\cdot}15\ (2)$ Å, $\beta = 118{\cdot}65\ (3)°$, $Z = 4$, $D_x = 1{\cdot}74$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 98{\cdot}4$ cm^{-1}. Each six-coordinate Mn atom is bonded to a phenanthroline ligand and is also linked through $H_2PO_2^-$ groups to four other Mn atoms so that a puckered net is obtained parallel to the *bc* plane.

Introduction. The title compound was obtained by the method of Sala-Pala, Kergoat & Everchais (1972) as yellow laths elongated along **c**. Equi-inclination Weissenberg photographs of the levels 0–7*kl* and *h*0–7*l* were recorded from two fragments (each 0·1 × 0·3 × 0·3 mm), and were scanned by the SRC Microdensitometer Service, Daresbury. The structure was solved by the heavy-atom method after the data had been corrected for absorption. Twelve of the strongest peaks in a difference synthesis, weighted to emphasize low-angle reflections, at *R* 0·069 were clearly assignable to the H atoms; they occurred at distances of 1·38 to 1·55 Å from P and 0·94 to 1·17 Å from C. In the last cycles, the H atoms were included at calculated positions (d_{P-H} 1·40, d_{C-H} 1·05 Å, U_H 0·05 Å^2). Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms converged at *R* 0·063, R_w 0·065 [weights given by $w = 1/(1 + 0{\cdot}0116F^2)$; 190 parameters; 1657 unique reflections above background]. The final atomic coordinates are given in Table 1, and distances and angles in Table 2. Fig. 1 illustrates the numbering scheme. G. M. Sheldrick's *SHELX* 76 system was used in all calculations.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Lending Library Division as Supplementary Publication No. SUP 33856 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.