Acta Cryst. (1984). C**40**, 1499–1502

The Structure of Dicalcium Potassium Heptahydrogen Tetrakis(phosphate) Dihydrate, $Ca_2KH_7(PO_4)_4.2H_2O$, by X-ray and Neutron Diffraction

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(*Received* 20 *January* 1984; *accepted* 3 *May* 1984)

Abstract. $M_r = 542\cdot25$, triclinic, $a = 5\cdot676$ (1), $b = 12\cdot210$ (2), $c = 6\cdot292$ (1) Å, $\alpha = 104\cdot10$ (3), $\beta = 115\cdot16$ (2), $\gamma = 84\cdot25$ (2)°, $V = 382\cdot8$ (6) Å^3, $Z = 1$, $D_x = 2\cdot352$ Mg m^{-3}, $\mu = 1\cdot51$ mm^{-1}, $F(000) = 274$ (X-rays), $\mu = 0\cdot14$ mm^{-1}, $F(000) = 96\cdot5$ fm (neutrons), $T = 298$ K. For X-rays, space group $P\bar{1}$, Mo $K\alpha$, $\lambda = 0\cdot7107$ Å, $R = 0\cdot024$ for 2040 independent observed reflections. For neutrons, space group $P1$, $\lambda = 1\cdot273$ Å, $R = 0\cdot051$ for 1383 independent observed reflections. The structure is isomorphous with $Ca_2(NH_4)H_7(PO_4)_4.2H_2O$. Although K could occupy a center of symmetry, it apparently does not, and two of the three hydrogen bonds that would cross centers of symmetry in $P\bar{1}$ are also markedly asymmetric. Because of the greater sensitivity of neutrons to hydrogen atoms, it is concluded that the correct space group is $P1$.

Introduction. In a study of the compound $Ca_2(NH_4)H_7(PO_4)_4.2H_2O$ (Takagi, Mathew & Brown, 1980) it was found that the structure could be successfully refined in space group $P\bar{1}$, although this required the ammonium ion to be statistically disordered in the vicinity of a center of symmetry. However, the resulting structure contained three hydrogen bonds that crossed centers of symmetry that were unusually long ($\geq 2\cdot50$ Å) for symmetric hydrogen bonds. It was not possible using X-ray diffraction to study the hydrogen positions to determine whether the bonds were truly symmetric, were disordered across the centers of symmetry, or whether the structure was actually noncentrosymmetric. Single crystals of the ammonium compound large enough for neutron diffraction measurements were not available, but some large single crystals of an isomorphous compound with potassium substituted for the ammonium were obtained. This study was undertaken to determine the symmetry of the compound and the configuration of the hydrogen bonds.

Experimental. Crystals prepared by procedure of Flatt, Brunisholz & Chapuis-Gottreux (1951). Cell parameters by least-squares fit of 2θ values of 15 reflections in the range 48–54°, measured at both positive and negative settings on a Picker X-ray diffractometer using graphite-monochromated Mo $K\alpha_1$ radiation ($\lambda = 0\cdot70932$ Å). X-ray diffraction data collected using θ–2θ scan technique. Diffractometer control programs of Lenhert (1975). Neutron diffraction data collected on four-circle neutron diffractometer at NBS research reactor using a procedure described previously (Prince, 1972), in which a preliminary measurement of peak height is made, and only those reflections whose peak heights exceed background by at least 2σ are considered to be observed and measured further by a θ–2θ scan. The cell parameters from the X-ray measurements were used. Crystal and experimental data are given in Table 1. Intensities reduced to structure factors, structure refined using *RFINE*4 (Finger & Prince, 1975). $\sum w_i(|F_{oi}| - |F_{ci}|)^2$ minimized. Scattering factors and anomalous dispersion corrections for X-rays and scattering factors for neutrons from *International Tables for X-ray Crystallography* (1974). Patterson map and electron density maps confirmed that the structures of the potassium and ammonium salts were isomorphous. Therefore, atomic coordinates of $Ca_2(NH_4)H_7(PO_4)_4.2H_2O$ (Takagi *et al.*, 1980) were used as initial parameters in refinement of X-ray data. Neutron refinement weights determined initially by $w_i = 1/[\sigma_{ci}^2 + (0\cdot025F_{oi})^2]$ where σ_{ci}^2 is variance of *i*th structure factor based on counting statistics. In later stages of refinement robust/resistant weighting scheme used (Nicholson, Prince, Buchanan & Tucker, 1983): $w'_i = w_i[1 - (r_i/s)^2]^2$ for $|r_i/s| \leq 1$, $w'_i = 0$ otherwise. r_i denotes $w_i^{1/2}(|F_{oi}| - |F_{ci}|)$, s is resistant measure of scale chosen to be $9|r_i|_m$, where $|r_i|_m$ is median of absolute values of r_i. Initial parameters from preliminary refinement of X-ray data. Four different versions of model used: (1) space group

0108-2701/84/091499-04$01.50

Table 1. *Crystal, experimental and final refinement data for* $Ca_2KH_7(PO_4)_4.2H_2O$

	X-ray	Neutron
Crystal dimensions (mm)	0·23 × 0·22 × 0·09	5·0 × 3·0 × 1·0
Wavelength (Å)	0·7107	1·273
2θ max (°)	60	116
Scan rate	0·5° min^{-1}	Variable (see text)
Number of unique reflections	2145	1872
Number of observable reflections	2040 [$>3\sigma(F_o)$]*	1398
Range of *h, k, l*	0–7,−16–17,−7–7	0–7,−15–16,−8–7
Absorption correction range	1·13–1·34†	
Space group used	$P\bar{1}$	$P1$
Number of variables	138	227
R	0·024	0·051 (1383 reflections)
wR	0·042	0·060
w^{-1}	$\sigma^2(F_o)+(0{\cdot}02F_o)^2$	See text
S	1·77	2·15
Max. Δ/σ	1·2	0·10
Av. Δ/σ	0·1	0·03
$\Delta\rho$	<0·4 e $Å^{-3}$	0·02‡
Extinction parameter§	2·7 (4) × 10^{-5}	9 (3) × 10^{-7}

* Calculated from counting statistics.

† The absorption correction was applied using *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). For neutrons no absorption corrections were applied.

‡ The unit is density of nuclei with scattering length 10 fm.

§ Zachariasen (1967). For neutrons the parameter is the product $r \times \bar{t}$.

$P\bar{1}$, with potassium atom on center of symmetry; (2) space group $P\bar{1}$, with half a potassium atom in each of two positions symmetrically displaced from center; (3) space group $P1$, with potassium atom in single off-center position and with temperature factors of pairs of atoms related by center in models 1 and 2 constrained to be equal; and (4) space group $P1$, with all temperature factors unconstrained. Because of well known numerical problems with refinement in non-centrosymmetric space groups of structures that are almost centrosymmetric first few cycles of model 3 utilized an alternative more stable algorithm of the type known as a quasi-Newton algorithm (Broyden, 1972). Table 2 is a summary of the R indices and numbers of parameters for all four models.

Discussion. The final atomic parameters for the X-ray and neutron refinements are listed in Tables 3 and 4, respectively. Inasmuch as the structures of $Ca_2(NH_4)H_7(PO_4)_4.2H_2O$ and $Ca_2KH_7(PO_4)_4.2H_2O$ are isomorphous, and the structure of the former has been described in detail (Takagi *et al.*, 1980), the discussion will be limited to the bonds involving hydrogen atoms, as determined in the neutron refinement.

As can be seen in Table 2, each of the three lower symmetry models shows an improvement in the fit, relative to the next more restrictive model. In each case the R ratio test (Hamilton, 1965) shows that the probability of observing that improvement by chance is essentially zero (less than 10^{-6}). Model 4, however, has one anisotropic temperature factor matrix that is not positive definite, and the refined position parameters are not markedly different from those of model 3. For this reason further discussion of the detailed structure will be based on the parameters of model 3. Table 5 gives a list of selected bond distances for both refinements,* and Table 6 gives details of hydrogen-bond configurations. Fig. 1 is an overall view of the structure.

The immediately apparent salient feature of model 1 was a very large anisotropy in the temperature factor of the potassium atom, and the fact that there was substantial improvement in the fit in going to model 2 with only three additional parameters is a strong

Table 2. *Summary of the R indices in the neutron diffraction refinement, the number of reflections included in the refinement and the number of parameters for each of four models of* $Ca_2KH_7(PO_4)_4.2H_2O$

Model	Number of reflections	Number of parameters	R (%)	R_w (%)
(1) $P\bar{1}$–K on center	1381	170	5·9	7·0
(2) $P\bar{1}$–K split	1381	173	5·7	6·7
(3) $P1$–TF's constrained	1383	227	5·1	6·0
(4) $P1$–unconstrained	1379	323	4·5	5·2

Table 3. *Refined position parameters and equivalent isotropic thermal parameters for the X-ray refinement of* $Ca_2KH_7(PO_4)_4.2H_2O$

E.s.d.'s for the least significant digits are given in parentheses.

	x	y	z	B^*_{eq} ($Å^2$)
Ca	−0·00076 (5)	0·09902 (2)	0·29829 (5)	0·90 (2)
K†	0·49694 (28)	0·53752 (14)	−0·01372 (30)	4·84 (8)
P(1)	0·15159 (8)	0·63698 (3)	0·37840 (8)	1·19 (2)
P(2)	0·49717 (7)	−0·09738 (3)	0·21138 (6)	0·84 (2)
O(11)	0·1048 (3)	0·5952 (1)	0·1098 (2)	2·02 (7)
O(12)	0·1388 (2)	0·7647 (1)	0·4351 (2)	1·27 (5)
O(13)	0·4220 (3)	0·5984 (1)	0·5390 (3)	2·25 (6)
O(14)	−0·0615 (3)	0·5853 (1)	0·4134 (3)	2·04 (7)
O(21)	0·2440 (2)	−0·0352 (1)	0·1426 (2)	1·25 (6)
O(22)	0·7464 (2)	−0·0320 (1)	0·3192 (2)	1·21 (5)
O(23)	0·5312 (2)	−0·1685 (1)	0·3986 (2)	1·46 (6)
O(24)	0·4632 (3)	−0·1833 (1)	−0·0326 (2)	1·84 (6)
O(3)	0·1434 (3)	0·2477 (1)	0·1743 (2)	1·55 (6)
H(23)	0·392 (5)	−0·191 (2)	0·396 (4)	2·8 (5)
H(24)	0·570 (6)	−0·205 (3)	−0·059 (5)	3·4 (7)
H(31)	0·034 (5)	0·284 (2)	0·052 (4)	2·5 (5)
H(32)	0·259 (6)	0·303 (3)	0·299 (6)	5·2 (7)
H(11)	0·0	0·5	0·0	8·6 (13)
H(13)	0·5	0·5	0·5	13·2 (15)
H(14)	0·0	0·5	0·5	3·4 (8)

* Hamilton (1959).

† Atom is statistically disordered across a center of symmetry. An occupancy factor of 0·5 was used in all calculations.

* Lists of structure factors, anisotropic temperature factors and O–P–O angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39453 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Refined position parameters and equivalent isotropic thermal parameters for the neutron refinement of* $Ca_2KH_7(PO_4)_4.2H_2O$

E.s.d.'s for the least significant digits are given in parentheses. K was held fixed to define the origin.

	x	*y*	*z*	B^*_{eq}(Å^2)
Ca	−0·0032 (21)	0·0991 (12)	0·3005 (20)	0·87 (3)
Ca^{i}	−0·0019 (21)	−0·0980 (12)	−0·2961 (21)	0·87 (3)
K	0·4948	0·5377	−0·0154	4·34 (25)
P(1)	0·1372 (21)	0·6348 (12)	0·3768 (20)	1·12 (4)
P(1^{i})	−0·1664 (21)	0·3606 (12)	−0·3812 (21)	1·12 (4)
P(2)	0·4926 (20)	−0·0954 (12)	0·2103 (20)	0·75 (3)
P(2^{i})	−0·5014 (20)	0·0990 (12)	−0·2123 (20)	0·75 (3)
O(11)	0·0944 (22)	0·5954 (11)	0·1071 (20)	1·93 (4)
O(11^{i})	−0·1148 (22)	0·4055 (11)	−0·1127 (20)	1·93 (4)
O(12)	0·1460 (20)	0·7671 (11)	0·4505 (20)	1·03 (4)
O(12^{i})	−0·1335 (20)	0·2372 (11)	−0·4209 (20)	1·03 (4)
O(13)	0·4149 (21)	0·5951 (11)	0·5394 (22)	2·24 (4)
O(13^{i})	−0·4285 (21)	0·3986 (11)	0·4605 (22)	2·24 (4)
O(14)	−0·0652 (21)	0·5852 (12)	0·4108 (23)	2·15 (4)
O(14^{i})	0·0576 (21)	0·4146 (12)	−0·4159 (23)	2·15 (4)
O(21)	0·2406 (20)	−0·0388 (11)	0·1432 (20)	1·16 (3)
O(21^{i})	−0·2483 (20)	0·0317 (11)	−0·1418 (21)	1·16 (3)
O(22)	0·7443 (19)	−0·0314 (11)	0·3215 (20)	1·18 (3)
O(22^{i})	0·2516 (20)	0·0325 (11)	−0·3178 (20)	1·18 (3)
O(23)	0·5312 (20)	−0·1668 (12)	0·3912 (20)	1·27 (4)
O(23^{i})	0·4682 (20)	0·1705 (12)	−0·4055 (20)	1·27 (4)
O(24)	0·4623 (20)	−0·1836 (12)	−0·0305 (20)	1·74 (4)
O(24^{i})	−0·4666 (21)	0·1831 (12)	0·0342 (20)	1·74 (4)
O(3)	0·1428 (21)	0·2463 (11)	0·1761 (21)	1·48 (4)
O(3^{i})	−0·1437 (21)	−0·2507 (11)	−0·1728 (21)	1·48 (4)
H(23)	0·366 (3)	−0·1881 (14)	0·405 (3)	2·09 (6)
H(23^{i})	−0·366 (3)	0·1913 (14)	−0·418 (3)	2·09 (6)
H(24)	0·625 (3)	−0·1973 (14)	−0·064 (3)	2·58 (8)
H(24^{i})	0·385 (3)	0·2058 (15)	0·074 (3)	2·58 (8)
H(31)	0·025 (3)	0·2966 (16)	0·063 (3)	3·09 (7)
H(31^{i})	−0·039 (3)	−0·2909 (16)	−0·063 (3)	3·09 (7)
H(32)	0·238 (4)	0·3048 (16)	0·314 (3)	3·96 (11)
H(32^{i})	−0·262 (4)	−0·2992 (16)	−0·315 (3)	3·96 (11)
H(11)	−0·034 (3)	0·4928 (21)	−0·015 (4)	3·63 (19)
H(13)	0·469 (3)	0·5106 (17)	0·509 (3)	3·23 (22)
H(14)	0·003 (4)	0·5037 (25)	0·509 (4)	3·80 (14)

* Hamilton (1959).

Table 5. *Selected bond distances in* $Ca_2KH_7(PO_4)_4.2H_2O$ (Å)

E.s.d.'s for the least significant digits are given in parentheses.

	X-ray	Neutron (1)	Neutron (2)
Ca–O(12)	2·386 (1)	2·424 (10)	2·354 (10)
Ca–O(21)	2·344 (1)	2·370 (11)	2·317 (11)
Ca–O(21^{i})	2·473 (1)	2·485 (9)	2·459 (10)
Ca–O(22)	2·315 (1)	2·310 (9)	2·315 (9)
Ca–O(22^{i})	2·513 (1)	2·507 (9)	2·509 (9)
Ca–O(23)	2·608 (1)	2·611 (10)	2·608 (9)
Ca–O(24)	2·704 (2)	2·707 (10)	2·717 (10)
Ca–O(3)	2·471 (1)	2·462 (10)	2·502 (10)
K–O(11)	2·635 (3)	2·676 (11)	
K–O(11^{i})	2·838 (2)	2·801 (11)	
K–O(13)	2·931 (2)	2·891 (12)	
K–O(14)	2·765 (2)	2·757 (12)	
K–O(14^{i})	2·881 (2)	2·891 (13)	
P(1)–O(11)	1·553 (1)	1·564 (9)	1·549 (9)
P(1)–O(12)	1·514 (1)	1·567 (9)	1·472 (9)
P(1)–O(13)	1·539 (2)	1·575 (9)	1·499 (9)
P(1)–O(14)	1·535 (2)	1·464 (9)	1·604 (9)
P(2)–O(21)	1·497 (1)	1·461 (9)	1·528 (9)
P(2)–O(22)	1·498 (1)	1·499 (8)	1·496 (9)
P(2)–O(23)	1·565 (1)	1·529 (9)	1·606 (9)
P(2)–O(24)	1·581 (1)	1·583 (10)	1·583 (10)

Table 6. *Geometry of the hydrogen bonds in* $Ca_2KH_7(PO_4)_4.2H_2O$

E.s.d.'s for the least significant digits are given in parentheses.

O–H···O	O–H (Å)	H···O (Å)	O···O (Å)	∠O–H···O (°)
From the X-ray refinement				
O(3)–H(31)···O(11)	0·94 (2)	1·91 (2)	2·801 (2)	157·9 (23)
O(3)–H(32)···O(13)	0·95 (4)	2·01 (4)	2·892 (2)	154·6 (32)
O(23)–H(23)···O(12)	0·85 (3)	1·71 (3)	2·563 (2)	171·6 (26)
O(24)–H(24)···O(3)	0·71 (4)	2·02 (4)	2·720 (2)	169·7 (27)
O(11)–H(11)···O(11)	1·26	1·26	2·514 (2)	180
O(13)–H(13)···O(13)	1·24	1·24	2·483 (2)	180
O(14)–H(14)···O(14)	1·24	1·24	2·486 (2)	180
From the neutron refinement				
O(3)–H(31)···O(11^{i})	1·027 (15)	1·839 (15)	2·848 (10)	166·7 (12)
O(3)–H(32)···O(13^{i})	0·967 (18)	2·045 (19)	2·858 (10)	140·6 (17)
O(3^{i})–H(31^{i})···O(11)	0·912 (15)	1·861 (15)	2·746 (10)	162·8 (14)
O(3^{i})–H(32^{i})···O(13)	0·957 (18)	2·081 (19)	2·920 (10)	145·5 (17)
O(23)–H(23)···O(12)	1·040 (12)	1·569 (12)	2·601 (8)	171·2 (11)
O(24)–H(24)···O(3^{i})	1·023 (14)	1·727 (14)	2·729 (10)	165·3 (12)
O(23^{i})–H(23^{i})···O(12^{i})	1·039 (12)	1·492 (12)	2·525 (8)	172·2 (13)
O(24^{i})–H(24^{i})···O(3)	0·972 (14)	1·736 (14)	2·704 (10)	173·9 (13)
O(11)–H(11)···O(11^{i})	1·388 (20)	1·126 (21)	2·509 (4)	173·3 (16)
O(13)–H(13)···O(13^{i})	1·041 (17)	1·447 (17)	2·482 (4)	171·9 (14)
O(14)–H(14)···O(14^{i})	1·241 (30)	1·250 (30)	2·487 (4)	173·4 (19)

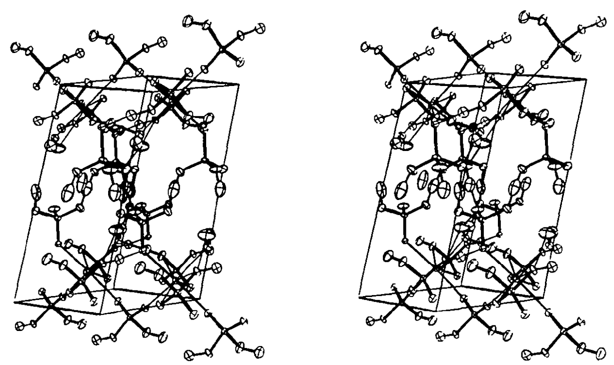

Fig. 1. Stereoscopic pair (Johnson, 1965) showing the unit cell of $Ca_2KH_7(PO_4)_4.2H_2O$.

indication that the potassium does not occupy a single potential well located at the center of symmetry. Three hydrogen atoms, H(11), H(13), and H(14), occupy centers of symmetry in model 2 but not in model 3. As was expected, in view of the long O–O distance, two of these hydrogen bonds refined to asymmetric configurations. H(14), however, remained very close to the center of the bond, although one of the oxygen atoms became unusually far away from its associated phosphorus atom. To determine whether this might be due to a false minimum, the hydrogen atom was displaced to a position 1·0 Å away from the oxygen with the long P–O distance, on the assumption that this oxygen was more likely to be the donor, and the refinement was repeated. In two cycles no other atom moved significantly, but H(14) returned to its position close to the center of the bond.

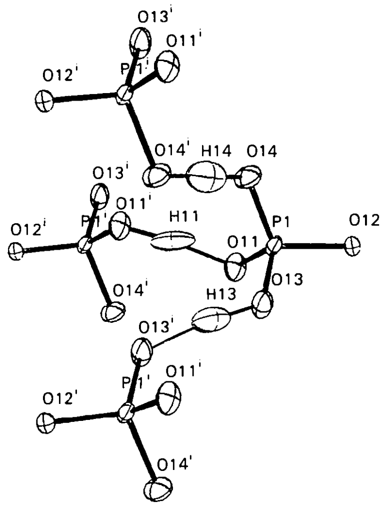

Fig. 2. The three hydrogen bonds that cross pseudo centers of symmetry. O(14)—H(14)—O(14^{i}) is still nearly symmetric in *P*1. All of the hydrogen atoms have large amplitudes of thermal motion parallel to the bond.

Fig. 2 shows the three hydrogen bonds involving the hydrogen atoms that occupy centers of symmetry in models 1 and 2. It is apparent that all three of these hydrogen atoms have large amplitudes of thermal vibration nearly parallel to the O—O vector, which implies that the potential wells, whether they have single or double minima, are rather flat in that direction.

This investigation was supported in part by Research Grant DE 05030-05 to the American Dental Association Health Foundation by the National Institute of Dental Research and is part of the Dental Research Program conducted by the National Bureau of Standards in cooperation with the American Dental Association Health Foundation.

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Trithallium Tetraselenophosphate, Tl_3PSe_4, and Trithallium Tetrathioarsenate, Tl_3AsS_4, by Neutron Time-of-Flight Diffraction

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(*Received* 2 *September* 1983; *accepted* 25 *April* 1984)

Abstract. Room-temperature (293 K) single-crystal structure determinations of the isostructural materials Tl_3PSe_4 and Tl_3AsS_4 were performed at the Los Alamos National Laboratory Pulsed Neutron Facility. For Tl_3PSe_4: $M_r = 959{\cdot}92$, *Pcmn*, $a = 9{\cdot}276\,(1)$, $b = 11{\cdot}036\,(2)$, $c = 9{\cdot}058\,(1)$ Å, $V = 927{\cdot}27$ Å^3, $Z = 4$, $D_m = 6{\cdot}87\,(2)$, $D_x = 6{\cdot}876$ Mg m^{-3}, $\lambda_{neutron} = 0{\cdot}5{\rightarrow}5{\cdot}2$ Å, $F(000) = 252{\cdot}5$ fm. For Tl_3AsS_4: $M_r = 816{\cdot}29$, *Pcmn*, $a = 9{\cdot}084\,(3)$, $b = 10{\cdot}877\,(3)$, $c = 8{\cdot}877\,(3)$ Å, $V = 877{\cdot}11$ Å^3, $Z = 4$, $D_m = 6{\cdot}18\,(2)$, $D_x = 6{\cdot}181$ Mg m^{-3}, $\lambda_{neutron} = 0{\cdot}5{\rightarrow}5{\cdot}2$ Å, $F(000) = 177{\cdot}2$ fm. For Tl_3PSe_4 (Tl_3AsS_4), 1929 (1013) reflections were measured with $I > 3\sigma(I)$ and refined by full-matrix least squares to $R(F) = 0{\cdot}061$ (0·063). Results on atomic refinement from this study represent an order of magnitude increase in precision over

