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The Crystal Structure of $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$

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$\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ crystallizes in the orthorhombic unit cell $a=7.146$ (1), $b=11.696$ (2), $c=7.100$ (2) Å at 25°C with cell contents of $2[\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}]$. The density calculated from the X-ray data is 2.027 g.cm^{-3} ; that calculated from the refractive indices is 2.10 g.cm^{-3} . The structure has been refined to $R_w=0.037$, $R=0.043$ in space group $Cm2m$, using 1023 observed reflections measured on an automated diffractometer and corrected for absorption. Allowance was made for anomalous dispersion and secondary isotropic extinction. All ions in $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ are completely hydrated. Ca coordinates to eight water oxygen atoms with $\text{Ca} \cdots \text{O}$ distances in the range 2.460 (5) to 2.490 (3) Å. K coordinates to eight water oxygen atoms with $\text{K} \cdots \text{O}$ distances ranging from 2.756 (3) to 2.960 (7) Å. The coordination polyhedron of Ca shares one face of four water molecules and two edges with neighboring coordination polyhedra of K. Each oxygen atom of the AsO_4 ion is the acceptor in hydrogen bonds from four water molecules and forms no bonds with the cations. The two crystallographically different As–O distances in the AsO_4^{3-} ion are 1.682 (4) and 1.684 (4) Å when uncorrected for thermal motion, and 1.690 and 1.692 Å with the riding model correction. The structure of $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ is related to that of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, struvite. This structural type may be common to several calcium phosphates and related compounds.

Introduction

In crystallization, nucleation is an important step which could conceivably control the identities and forms of materials that grow to macroscopic sizes. For various reasons (Dickens & Brown, 1970), studies of hydrates may give valuable clues to the existence of possible precursors or nuclei of crystallization in aqueous environments. In the formation of inorganic deposits *in vivo*, hydration of ions is likely to play a significant role, and the formation of ion pairs or higher complexes may be important. We found in our study of $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ (Dickens & Brown, 1970) that in the crystal structure, the Ca^{2+} and CO_3^{2-} ions are all in $[\text{Ca}^{2+}, \text{CO}_3^{2-}]^0$ ion pairs which are completely sur-

rounded by water molecules. To examine the hydration of Ca and the possible retention in the solid state of ion complexes involving XO_4 ions, in this case AsO_4^{3-} , we have determined the crystal structure of $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$.

Data collection and structure refinement

$\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ was prepared by mixing 20 cm³ of 0.1 M.l⁻¹ CaCl_2 solution, 25 cm³ 1.0 M.l⁻¹ tripotassium citrate solution and 10 cm³ 3.0 M.l⁻¹ KOH solution at 0°C and then adding 10 cm³ 0.2 M.l⁻¹ K_2HAsO_4 solution. The resultant mixture was kept at 0°C; precipitation of $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ began after about two hours. This procedure is an adaptation of that given for $\text{CaNH}_4\text{PO}_4 \cdot 7\text{H}_2\text{O}$ by Lehr, Brown, Frazier, Smith & Thrasher (1967).

The crystal used in the data collection was a rectangular plate with dimensions 0.06 × 0.10 × 0.12

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mm. It was mounted on the goniometer using the procedure described by Dickens & Bowen (1971a).

Formula (ideal): $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$.

Cell at 25°C: orthorhombic.

$a = 7.146$ (1) Å

$b = 11.696$ (2)

$c = 7.100$ (2)

Volume = 593.4 Å³.

Space-group $Cm2m(C_{2v}^4)$; cell contents
2[CaKAsO₄·8H₂O].

Reciprocal lattice extinctions: $h+k=2n+1$ for hkl .

Density calculated from unit cell = 2.027 g.cm⁻³.

Density calculated from refractive indices = 2.10 g.cm⁻³ (TVA, unpublished data).

In general, the data collection and data processing procedure given by Dickens & Bowen (1971a, b) were followed. The θ - 2θ scans here were carried out at 0.5° per min for 2θ . Each background was counted for 40 sec. Absorption corrections were made assuming $\mu(\text{Mo}) = 39.6$ cm⁻¹. The maximum and minimum transmission factors were 0.83 and 0.66 respectively. 2163 reflections were collected from the hkl and $\bar{h}kl$ octants of the reciprocal lattice and were merged into a unique set of 1071, of which 1023 are 'observed' and 48 are 'unobserved'. Equivalent reflections agreed within 3.4% on average. 'Unobserved' reflections are those less than $2\sigma(I)$ above background.

The structure of CaKAsO₄·8H₂O was solved from a sharpened Patterson map [calculated from the $E^2 - 1$ coefficients, where E is the quasi-normalized structure factor (Dickinson, Stewart & Holden, 1966)] and from subsequent F_o electron density syntheses. The scattering factors used were those of the neutral atoms; they were taken from *International Tables for X-ray Crystallography* (1962) and McWeeny (1951) for the XRAY67 (Stewart, 1967) refinements and from Cromer & Mann (1968) for the refinements using the program *RFINE*, written by L. W. Finger of the Carnegie Institute of Washington. The structure with hydrogen atoms excluded was refined isotropically to $R_w = 0.067$, $R = 0.068$ using XRAY67. The quantity minimized was $\sum_w(F_o -$

$F_c)^2$. Unobserved reflections calculating more than $2\sigma(F_{hkl})$ were included. Three cycles of anisotropic refinement varying all unconstrained parameters decreased R_w to 0.054 and R to 0.056.

A difference electron-density synthesis was calculated. The hydrogen positions were taken from peaks equivalent to 0.5 to 0.9 electrons within 1.2 Å of the water oxygen atoms. The structure including hydrogen atoms with variable positional parameters but with hydrogen thermal parameters fixed at $B = 1.0$ Å² was then refined anisotropically to $R_w = 0.040$, $R = 0.047$ in three cycles using the least-squares program *RFINE*. Correction was made for secondary isotropic extinction. Although the environments of the oxygen atoms in the AsO₄ group are not very different, the surprising result that the two crystallographically different As...O distances were 1.664 (4) and 1.701 (4) Å was obtained. After a correction for anomalous dispersion was included in the refinement, the As...O distances became essentially equal, as would be expected from a consideration of their similar environments. The values of f' and f'' were taken from Cromer (1965). The parameters from the third cycle ($R_w = 0.037$, $R = 0.043$) of this series of refinements are given in Table 1. (The values for refinement of the other enantiomorph are $R_w = 0.049$, $R = 0.054$.) The observed and calculated structure factors are given in Table 2. The average shift/error in the last cycle was 0.19 excluding hydrogen parameters and 0.35 for all parameters. The standard deviation of an observation of unit weight, $[\sum_w(|F_o| - |F_c|)^2 / (1071 - 57)]^{1/2}$, was 1.60 which has been applied to the standard deviations quoted in the tables. The largest correlation coefficient was 0.41 between (B_{22} , B_{12}) of O(4); all others were below 0.17. Because the isotropic secondary extinction parameter refined to -0.00000100 (7) cm, it was constrained to zero in the final refinements.

The largest peaks in a weighted difference electron-density synthesis calculated at this stage were equivalent to about $\frac{1}{2}$ an electron between As and O(1), and about $\frac{1}{3}$ an electron at 0.5, 0.35, 0.25. Because of its proximity to As and O(1), the former peak cannot be attributed to an atom. The latter peak is in a void in the structure, but is, however, only 2.30 Å from O(5),

Table 1. Atomic parameters of CaKAsO₄·8H₂O

Figures in parentheses are standard errors in last significant figure quoted, and were computed in the final cycle of full-matrix least-squares refinement.

Thermal parameters are in the form $\exp[-\frac{1}{4}(a^*2B_{11}h^2 + b^*2B_{22}k^2 + c^*2B_{33}l^2 + 2a^*b^*B_{12}hk + 2a^*c^*B_{13}hl + 2b^*c^*B_{23}kl)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca mm^*	0.0	0.3750 (1)	0.5	1.16 (4)	1.20 (5)	1.04 (5)	-	-	-
K mm	0.5	0.1877	0.5	1.40 (5)	1.94 (7)	2.33 (7)	-	-	-
As mm	0.0	0.0	0.0	0.89 (2)	0.77 (2)	0.87 (2)	-	-	-
O(1) m	0.0	0.0793 (4)	0.1977 (5)	1.9 (1)	1.4 (1)	1.2 (1)	-	-	-0.4 (1)
O(2) m	0.3027 (5)	0.4212 (4)	0.0	1.2 (1)	1.9 (2)	1.7 (1)	-0.5 (1)	-	-
O(3) m	0.5	0.0031 (6)	0.2235 (5)	1.9 (1)	2.4 (1)	1.4 (1)	-	-	-0.1 (2)
O(4) m	0.2228 (5)	-0.0003 (7)	0.5	1.6 (1)	3.2 (2)	1.8 (1)	1.0 (2)	-	-
O(5) l	0.2119 (4)	0.2697 (3)	0.2824 (4)	2.2 (1)	1.3 (1)	1.7 (1)	-0.1 (1)	0.09 (7)	-0.07 (8)

* Symmetry of atom site. Equivalent positions: x, y, z ; $-x, y, z$; $-x, y, -z$; $x, y, -z$; $\frac{1}{2} + x, \frac{1}{2} + y, z$; $\frac{1}{2} - x, \frac{1}{2} + y, z$; $\frac{1}{2} - x, \frac{1}{2} + y, -z$; $\frac{1}{2} + x, \frac{1}{2} + y, -z$.

Table 2. *Observed and calculated structure factors for $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$*

Columns are $h, 10F_o$, $10F_c$ and phase in millicycles. 'Unobserved' reflections are marked by *. F_c does not include corrections for extinction or anomalous dispersion. F_o and F_c are on an absolute scale.

2 705 734 0	9 227 232 0	10 103 97 0	H+0-0	H+5-4	2 327 321 67	8 169 181 958	H+0-7	H+11-2	H+12-10	4 77 101 41	H+17-2
1 470 1456 0	11 220 231 080		H+2-8	0 8161 1013 900	4 309 302 102	10 80 99 47					
0 755 770 0			H+1-4	2 143 115 124	5 357 314 971		H+2-2	1 261 275 958	1 325 325 52	1 124 114 46	H+14-9
10 444 446 0	1 193 191 27	0 251 276 916		4 100 455 5	5 152 157 988			5 148 144 982	5 274 274 71	2 404 40 24	
12 138 136 0	3 45 53 766	4 102 114 900		8 157 159 903	7 189 194 900		H+1-9	0 303 309 987	0 228 228 42		H+13-0
	7 40 38 851	8 192 190 924		10 137 125 921	11 71 79 984			2 215 215 984	2 228 228 42		
	11 36 44 961	12 107 102 897		13 36 35 950	14 161 160 928		H+0-8	4 164 157 910	8 217 230 71		
0 86 31 500			H+2-9	1 202 215 68	2 129 123 880	10 99 113 905		1 791 214 126	1 790 203 000	3 260 260 000	H+11-3
2 134 133 0			H+1-5	4 443 431 35	5 120 113 50		H+0-3	3 166 172 122	3 170 182 979	5 252 252 46	H+11-1
4 140 21 500	1 690 693 1	0 261 330 24		21170 1133 59	2 297 302 109			5 182 183 120	5 253 254 8		H+1-1
6 185 150 0	3 309 301 55	2 267 241 46		4 594 599 56	5 120 213 102		H+1-0	7 114 150 130	7 133 132 970	9 142 136 7	H+1-4
10 59 57 0	5 621 649 968	6 215 213 28		8 374 373 50	11 88 87 83		H+0-9	9 160 159 978	9 224 224 14	1 179 181 121	H+1-1
12 138 136 0	7 733 743 45	8 162 141 60		10 210 217 31				1 185 192 978	1 244 244 14	1 149 142 113	H+1-1
	9 208 210 983	10 117 102 897		12 141 140 65			H+0-5	3 156 155 920	3 175 177 46	4 262 262 958	H+1-1
0 688 681 0			H+2-10	1 300 297 964	1 300 297 964		H+0-1	7 105 115 920	7 115 115 920	9 220 212 969	H+1-5
2 359 358 500			H+1-6	2 189 286 9	2 189 286 9		H+0-4	9 160 159 978	9 224 224 14	1 179 181 121	H+1-1
4 140 21 500	1 690 693 1	0 261 330 24		4 594 599 56	5 120 213 102		H+0-2	1 105 105 920	1 115 115 920	1 179 181 121	H+1-1
6 185 150 0	3 309 301 55	2 267 241 46		8 374 373 50	11 88 87 83		H+0-1	3 166 172 122	3 170 182 979	5 252 252 46	H+1-1
10 59 57 0	5 621 649 968	6 215 213 28		10 210 217 31			H+0-0	5 182 183 120	5 253 254 8		H+1-1
12 138 136 0	7 733 743 45	8 162 141 60		12 141 140 65			H+0-0	7 114 150 130	7 133 132 970	9 142 136 7	H+1-4
	9 208 210 983	10 117 102 897		14 161 160 928			H+0-0	9 160 159 978	9 224 224 14	1 179 181 121	H+1-1
0 688 681 0			H+2-10	1 300 297 964	1 300 297 964		H+0-1	1 105 105 920	1 115 115 920	1 179 181 121	H+1-1
2 359 358 500			H+1-6	2 189 286 9	2 189 286 9		H+0-4	3 166 172 122	3 170 182 979	5 252 252 46	H+1-1
4 140 21 500	1 690 693 1	0 261 330 24		4 594 599 56	5 120 213 102		H+0-2	5 182 183 120	5 253 254 8		H+1-1
6 185 150 0	3 309 301 55	2 267 241 46		8 374 373 50	11 88 87 83		H+0-1	7 114 150 130	7 133 132 970	9 142 136 7	H+1-4
10 59 57 0	5 621 649 968	6 215 213 28		10 210 217 31			H+0-0	9 160 159 978	9 224 224 14	1 179 181 121	H+1-1
12 138 136 0	7 733 743 45	8 162 141 60		12 141 140 65			H+0-0	1 105 105 920	1 115 115 920	1 179 181 121	H+1-1
	9 208 210 983	10 117 102 897		14 161 160 928			H+0-0	3 166 172 122	3 170 182 979	5 252 252 46	H+1-1
0 688 681 0			H+2-10	1 300 297 964	1 300 297 964		H+0-1	5 182 183 120	5 253 254 8		H+1-1
2 359 358 500			H+1-6	2 189 286 9	2 189 286 9		H+0-4	7 114 150 130	7 133 132 970	9 142 136 7	H+1-4
4 140 21 500	1 690 693 1	0 261 330 24		4 594 599 56	5 120 213 102		H+0-2	9 160 159 978	9 224 224 14	1 179 181 121	H+1-1
6 185 150 0	3 309 301 55	2 267 241 46		8 374 373 50	11 88 87 83		H+0-1	1 105 105 920	1 115 115 920	1 179 181 121	H+1-1
10 59 57 0	5 621 649 968	6 215 213 28		10 210 217 31			H+0-0	3 166 172 122	3 170 182 979	5 252 252 46	H+1-1
12 138 136 0	7 733 743 45	8 162 141 60		12 141 140 65			H+0-0	5 182 183 120	5 253 254 8		H+1-1
	9 208 210 983	10 117 102 897		14 161 160 928			H+0-0	7 114 150 130	7 133 132 970	9 142 136 7	H+1-4
0 688 681 0			H+2-10	1 300 297 964	1 300 297 964		H+0-1	9 160 159 978	9 224 224 14	1 179 181 121	H+1-1
2 359 358 500			H+1-6	2 189 286 9	2 189 286 9		H+0-4	1 105 105 920	1 115 115 920	1 179 181 121	H+1-1
4 140 21 500	1 690 693 1	0 261 330 24		4 594 599 56	5 120 213 102		H+0-2	3 166 172 122	3 170 182 979	5 252 252 46	H+1-1
6 185 150 0	3 309 301 55	2 267 241 46		8 374 373 50	11 88 87 83		H+0-1	5 182 183 120	5 253 254 8		H+1-1
10 59 57 0	5 621 649 968	6 215 213 28		10 210 217 31			H+0-0	7 114 150 130	7 133 132 970	9 142 136 7	H+1-4
12 138 136 0	7 733 743 45	8 162 141 60		12 141 140 65			H+0-0	9 160 159 978	9 224 224 14	1 179 181 121	H+1-1
	9 208 210 983	10 117 102 897		14 161 160 928			H+0-0	1 105 105 920	1 115 115 920	1 179 181 121	H+1-1
0 688 681 0			H+2-10	1 300 297 964	1 300 297 964		H+0-1	3 166 172 122	3 170 182 979	5 252 252 46	H+1-1
2 359 358 500			H+1-6	2 189 286 9	2 189 286 9		H+0-4	5 182 183 120	5 253 254 8		H+1-1
4 140 21 500	1 690 693 1	0 261 330 24		4 594 599 56	5 120 213 102		H+0-2	7 114 150 130	7 133 132 970	9 142 136 7	H+1-4
6 185 150 0	3 309 301 55	2 267 241 46		8 374 373 50	11 88 87 83		H+0-1	9 160 159 978	9 224 224 14	1 179 181 121	H+1-1
10 59 57 0	5 621 649 968	6 215 213 28		10 210 217 31			H+0-0	1 105 105 920	1 115 115 920	1 179 181 121	H+1-1
12 138 136 0	7 733 743 45	8 162 141 60		12 141 140 65			H+0-0	3 166 172 122	3 170 182 979	5 252 252 46	H+1-1
	9 208 210 983	10 117 102 897		14 161 160 928			H+0-0	5 182 183 120	5 253 254 8		H+1-1
0 688 681 0			H+2-10	1 300 297 964	1 300 297 964		H+0-1	7 114 150 130	7 133 132 970	9 142 136 7	H+1-4
2 359 358 500			H+1-6	2 189 286 9	2 189 286 9		H+0-4	9 160 159 978	9 224 224 14	1 179 181 121	H+1-1
4 140 21 500	1 690 693 1	0 261 330 24		4 594 599 56	5 120 213 102		H+0-2	1 105 105 920	1 115 115 920	1 179 181 121	H+1-1
6 185 150 0	3 309 301 55	2 267 241 46		8 374 373 50	11 88 87 83		H+0-1	3 166 172 122	3 170 182 979	5 252 252 46	H+1-1
10 59 57 0	5 621 649 968	6 215 213 28		10 210 217 31			H+0-0	5 182 183 120	5 253 254 8		H+1-1
12 138 136 0	7 733 743 45	8 162 141 60		12 141 140 65			H+0-0	7 114 150 130	7 133 132 970	9 142 136 7	H+1-4
	9 208 210 983	10 117 102 897		14 161 160 928			H+0-0	9 160 159 978	9 224 224 14	1 179 181 121	H+1-1
0 688 681 0			H+2-10	1 300 297 964	1 300 297 964		H+0-1	1 105 105 920	1 115 115 920	1 179 181 121	H+1-1
2 359 358 500			H+1-6	2 189 286 9	2 189 286 9		H+0-4	3 166 172 122	3 170 182 979	5 252 252 46	H+1-1
4 140 21 500	1 690 693 1	0 261 330 24		4 594 599 56	5 120 213 102		H+0-2	5 182 183 120	5 253 254 8		H+1-1
6 185 150 0	3 309 301 55	2 267 241 46		8 374 373 50	11 88 87 83		H+0-1	7 114 150 130	7 133 132 970	9 142 136 7	H+1-4
10 59 57 0	5 621 649 968	6 215 213 28		10 210 217 31			H+0-0	9 160 159 978	9 224 224 14	1 179 181 121	H+1-1
12 138 136 0	7 733 743 45	8 162 141 60		12 141 140 65			H+0-0	1 105 105 920	1 115 115 920	1 179 181 121	H+1-1
	9 208 210 983	10 117 102 897		14 161 160 928			H+0-0	3 166 172 122	3 170 182 979	5 252 252 46	H+1-1
0 688 681 0			H+2-10	1 300 297 964	1 300 297 964		H+0-1	5 182 183 120	5 253 254 8		H+1-1
2 359 358 500			H+1-6	2 189 286 9	2 189 286 9		H+0-4	7 114 150 130	7 133 132 970	9 142 136 7	H+1-4
4 140 21 500	1 690 693 1	0 261 330 24		4 594 599 56	5 120 213 102		H+0-2	9 160 159 978	9 224 224 14	1 179 181 121	H+1-1
6 185 150 0	3 309 301 55	2 267 241 46		8 374 373 50	11 88 87 83		H+0-1	1 105 105 920	1 115 115 920	1 179 181 121	H+1-1
10 59 57 0	5 621 649 968	6 215 213 28		10 210 217 31			H+0-0	3 166 172 122	3 170 182 979	5 252 252 46	H+1-1
12 138 136 0	7 733 743 45	8 162 141 60		12 141 140 65			H+0-0	5 182 183 120	5 253 254 8		H+1-1
	9 208 210 983	10 117 102 897		14 161 160 928			H+0-0	7 114 150 130	7 133 132 970	9 142 136 7	H+1-4
0 688 681 0			H+2-10	1 300 297 964	1 300 297 964		H+0-1	9 160 159 978	9 224 224 14	1 179 181 121	H+1-1
2 359 358 500			H+1-6	2 189 286 9	2 189 286 9		H+0-4	1 105 105 920	1 115 115 920	1 179 181 121	H+1-1
4 140 21 500	1 690 693 1	0 261 33									

work we believed that the formula contained seven molecules of water, by analogy with $\text{CaNH}_4\text{AsO}_4 \cdot 7\text{H}_2\text{O}$. The thermal parameters of the oxygen atoms of the water molecules are fairly close to those of the oxygen atoms in the AsO_4 ion and thus the formula is $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ with no statistical vacancies. To confirm this, a sample of $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ was heated quickly (~ 1 min) to constant weight at 400°C ; a weight loss of 8.4 (3) moles of water per formula weight was obtained.

Three sets of hydrogen positions, (i) from the difference electron density synthesis, (ii) from the least-squares refinements, and (iii) positions assuming idealized water geometry, calculated as described in Dickens & Brown (1970), are given in Table 3. All distances and angles involving hydrogen in the tables or the text were obtained using the calculated hydrogen positions.

Description of the structure

The Ca, K and As atoms lie at the intersections of mirror planes parallel to (100) and (001). The oxygen atoms of the O(3) and O(4) water molecules lie on the (100) and (001) mirror planes respectively. The O(5) water molecule is in a general position.

All the ions in $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ are completely surrounded by water molecules, and thus there are no direct bonds between ions themselves. There are eight

water molecules in the coordination polyhedra of the Ca and K ions and 16 in the coordination polyhedron of the AsO_4 ion. Each of the water molecules in the structure is bonded to one Ca, one K and two AsO_4 ions. Each Ca coordination polyhedron shares a face of four water molecules with one K coordination polyhedron and edges with two other K coordination polyhedra.

The Ca ion environment

The environment of the Ca ion, which lies on the intersection of two mirror planes, is detailed in Table 4 and Fig. 1. The Ca ion is coordinated to eight oxygen atoms of water molecules arranged in an approximately square antiprism. The range of $\text{Ca}\cdots\text{O}$ distances, 2.460 to 2.490 Å, is unusually small and the bonding to all these oxygen atoms is of normal strength. The shortest $\text{O}\cdots\text{O}$ distance in this polyhedron is 2.789 Å for O(3) \cdots O(4). All other $\text{O}\cdots\text{O}$ distances are a little over 3 Å. The shortest $\text{Ca}\cdots\text{O}$ distances are to the approximate square of water oxygen atoms O(3ⁱ), O(3ⁱⁱ), O(4ⁱ), O(4ⁱⁱ) (see Caⁱ in Fig. 1), which is also part of the K ion environment. However, these oxygen atoms are the weakest bonded to K. The longest $\text{Ca}\cdots\text{O}$ bonds are to those water oxygen atoms in edges common to the coordination polyhedra of Caⁱ and Kⁱ. These oxygen atoms, O(5ⁱ) and O(5ⁱⁱ), are strongly to Kⁱ, though not as strongly as they are to Caⁱ.

Table 3. Probable positions of the hydrogen atoms in $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$

The calculated hydrogen positions were used to obtain distances mentioned in the tables and the text.

	Difference synthesis			Least-squares refinements			Calculated		
	x	y	z	x	y	z	x	y	z
H(1)	0.39	-0.02	0.14	0.395 (7)	0.001 (6)	0.150 (7)	0.394	-0.023	0.153
H(2)	0.14	0.00	0.43	0.139 (7)	-0.009 (6)	0.416 (7)	0.152	0.025	0.393
H(3)	0.25	0.31	0.21	0.236 (7)	0.320 (5)	0.192 (8)	0.235	0.316	0.174
H(4)	0.14	0.21	0.25	0.150 (9)	0.246 (6)	0.239 (10)	0.138	0.207	0.237

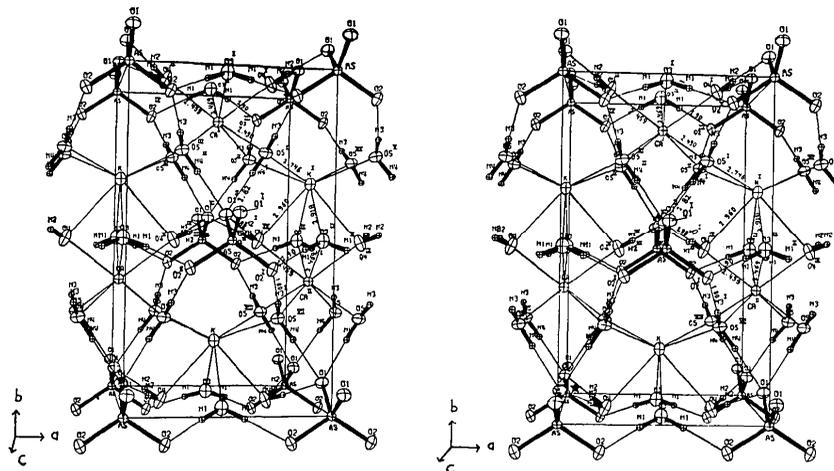


Fig. 1. A stereoscopic illustration of the crystal structure of $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$. The origin of the crystallographic coordinate system is marked by *. The atoms with Roman numerals are referred to in the table of interatomic distances; these Roman numerals are lower case in the text.

Table 4. *Interatomic distances and angles in*
 $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$

The cation environments		
Ca, O(4 ⁱ , 4 ⁱⁱ)		2.460 (5) Å
Ca, O(3 ⁱ , 3 ⁱⁱ)		2.470 (6)
Ca, O(5 ⁱ , 5 ⁱⁱ , 5 ⁱⁱⁱ , 5 ^{iv})		2.490 (3)
K, O(5 ⁱ , 5 ⁱⁱ , 5 ^v , 5 ^{vi})		2.746 (3)
K, O(3 ⁱⁱⁱ , 3 ^{iv})		2.919 (6)
K, O(4 ⁱⁱⁱ , 4 ^{iv})		2.960 (7)
The AsO ₄ group and its environment		
As—O(1,1)		1.682 (4)
		1.684 (a)
		1.690 (b)
As—O(2,2)		1.684 (4)
		1.685 (a)
		1.692 (b)
O(1)—As—O(1)		113.1 (3)°
O(1)—As—O(2)		107.5 (1)
O(2)—As—O(2)		113.7 (3)
O(1), O(1)		2.807 (7)
O(1), O(2)		2.715 (5)
O(2), O(2)		2.820 (7)
O(1), H(2 ⁱ , 2 ⁱⁱⁱ)		1.87
O(1), H(4 ⁱ , 4 ⁱⁱ)		1.81
O(1), O(5 ⁱⁱ , 5 ^{iv})		2.759 (4)*
O(1), O(4 ^{iv} , 4 ^v)		2.830 (4)*
O(2), H(1 ⁱ , 1 [†])		1.89
O(2), H(3 ⁱ , 3 [†])		1.81
O(2), O(5 ⁱⁱⁱ)		2.755 (4)*
O(2), O(3 ⁱⁱⁱ)		2.848 (4)*
The environments of the water molecules		
H(1), O(3), H(1)	O(3 ⁱⁱⁱ), Ca ⁱⁱ	2.469 (6) Å
	O(3 ⁱⁱⁱ), K ⁱ	2.918 (6)
	O(3 ⁱ), O(2 ⁱ , 2)	2.848 (4)*
	H(1), O(2 ⁱ)	1.89
	O(3)—H(1)—O(2)	175.7°
	O(2), O(3)—O(2)	98.8 (2)
H(2), O(4), H(2)	O(4 ^{iv}), Ca ⁱⁱ	2.459 (5)
	O(4 ^{iv}), K ⁱ	2.960 (7)
	O(4 ^{iv}), O(1, 1)	2.830 (4)*
	H(2), O(1)	1.87
	O(4)—H(2)—O(1)	175.6°
	O(1), O(4)—O(1)	98.7 (2)
H(3), O(5), H(4)	O(5 ⁱ), Ca ⁱ	2.490 (3)
	O(5 ⁱ), K ⁱ	2.746 (3)
	O(5 ⁱ), O(2 ^v)	2.755 (4)*
	O(5 ⁱ), O(1)	2.759 (4)*
	H(3), O(2 ^v)	1.81
	H(4 ⁱ), O(1)	1.81
	O(5)—H(3), O(2)	168.7°
	O(5)—H(4), O(1)	168.7
	O(1), O(5), O(2)	119.4 (1)

Figures in parentheses are standard deviations in the last digit and were calculated from the standard deviations in the atomic positional parameters. They include terms from the variance-covariance matrix.

(a) Lower bound and (b) riding model corrections for thermal motion (Busing & Levy, 1964).

* Hydrogen bond between these two oxygen atoms.

† These bonds may be seen in Fig. 1 if the environments of O(2) and O(2ⁱ) on the right hand side of the AsO₄ ion in the center of the figure are combined. O(2) and O(2ⁱ) are related by the *c* translation.

The K ion environment

The details of the environment of the K ion are

given in Table 4 and Fig. 1. K is bonded to eight water oxygen atoms arranged in a distorted square antiprism. As expected, K is relatively far (2.919, 2.960 Å) from water oxygen atoms O(3ⁱⁱⁱ), O(3^{iv}) and O(4ⁱⁱⁱ), O(4^{iv}) (see Kⁱ in Fig. 1), which are the closest water oxygen atoms to Caⁱⁱ. The Kⁱ ion instead forms stronger Kⁱ...O (2.746 Å) bonds to the O(5ⁱ), O(5ⁱⁱ), O(5^v), O(5^{vi}) water oxygen atoms in the face of the coordination polyhedron opposite the O(3), O(4) face. The shortest Kⁱ...Ca distance, Kⁱ...Caⁱⁱ = 3.66 Å, is along [010], across the shared face comprised of water oxygen atoms of types O(3ⁱⁱⁱ), O(3^{iv}) and O(4ⁱⁱⁱ), O(4^{iv}).

The AsO₄ group and its environment

The details of the AsO₄ group and its environment are given in Table 4. The two unique As—O distances are not significantly different, which is consistent with the lack of cations and very strong hydrogen bonds in the environment of the two oxygen atoms. The two O—As—O angles bisected by the mirror planes are significantly different from the other O—As—O angles. The reason seems to be that the force components of the hydrogen bonds from the water molecules are all such as to pull O(1) and O(2) away from the mirror planes to angles greater than the tetrahedral angle. The fact that the O(1)—As—O(2) angle of 107.5° is less than the tetrahedral angle is therefore a concomitant result. The AsO₄ group is extensively hydrogen bonded, O(1) and O(2) each being the acceptor in four hydrogen bonds (Table 4).

The environments of the water molecules

The environments of the water molecules are detailed in Table 4. Water oxygen atoms O(3) and O(4) lie on mirror planes; O(5) is in a general position. The water molecules in Fig. 1 and in Table 4 have been given the idealized geometry O—H = 0.958 Å and ∠H—O—H = 104.5°, as described in Dickens & Brown (1970). The hydrogen bonds were made as linear as possible in the calculation of the probable hydrogen positions. The smallest intermolecular H...H distances are 1.972 for H(4)...H(4'), 2.102 for H(1)...H(3), and 2.173 Å for H(1)...H(1') and H(2)...H(2'). All the oxygen atoms of the water molecules are bonded to the Ca and K ions and all the hydrogen atoms are hydrogen bonded to the oxygen atoms in the AsO₄ group. There is no hydrogen bonding between water molecules. The O(3) and O(4) water molecules are bonded strongly to Ca, less strongly to K, and are the donors in hydrogen bonds of average strength to O(2) and O(1) of the AsO₄ group. The O(5) water molecule is bonded slightly less strongly to Ca but more strongly to K than are O(3) and O(4), and appears to form slightly stronger hydrogen bonds to the AsO₄ group. As expected in order to minimize repulsions, the cations and hydrogen atoms are arranged in approximately tetrahedral directions about each water oxygen atom.

Discussion

The average As–O distance in $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ is 1.691 Å, corrected for thermal motion, and the individual As–O distances are equal within experimental error. The essentially equal As–O distances (obtained after correction for anomalous scattering) are expected from the close similarity of the environments of the oxygen atoms of the As–O group. Inclusion of anomalous scattering effects, therefore, resulted in a refinement of the As–O bond lengths from unreasonable to reasonable values.

Other recently determined structures which contain AsO_4 groups are $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$, haidingerite (Calleri & Ferraris, 1967), $2\text{H}_3\text{AsO}_4 \cdot \text{H}_2\text{O}$ (Worzala, 1968), $\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$, pharmacolite (Ferraris, 1969), $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Baur & Khan, 1970) and CaHAsO_4 , weilite (Ferraris & Chiari, 1970). The average As–O distance in $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$, 1.686 Å, is in good agreement with that observed in $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$, as are the averages, 1.690 and 1.679 Å, of the two crystallographically different AsO_4 groups in CaHAsO_4 . The average value in $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, 1.678 Å, is slightly shorter than the above values. The average value of As–O in the imprecisely determined structure of $2\text{H}_3\text{AsO}_4 \cdot \text{H}_2\text{O}$ is 1.652 Å, but the individual As–O distances range from 1.594 to 1.695 Å and undoubtedly suffer from systematic error due to uncorrected anomalous scattering. The environments of the AsO_4 groups in the above compounds differ from that in $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ by cation coordination and covalent bonding of H to the oxygen atoms of the AsO_4 group, so that comparison of individual As–O bond lengths is not meaningful. The average value of the As–O bond lengths seems to be essentially constant, as has been suggested for PO_4 groups by Cruickshank (1961) and denied by Baur & Khan (1970). It is now generally accepted that standard deviations in derived structural parameters may be too low by a factor in the range 1.4 to 2 for the positional parameters and 3 to 4 for the thermal parameters (Hamilton & Abrahams, 1970). When these factors are considered, the average values of As–O distances in AsO_4 groups may be considered to be constant within experimental error. The standard deviation of the average estimated from the spread of the individual values is typically in the range 0.01–0.02 Å for PO_4^{3-} groups in various structures. Thus the concept of constant average X–O distance in XO_4 groups may not be very useful.

The complete hydration of the Ca and K ions in $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ differs from that of another highly hydrated calcium salt, $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ (Dickens & Brown, 1970), where all cations are in $[\text{CaCO}_3]_0^0$ ion pairs. Evidence has been given for ion-complexes of calcium and phosphate ions in solution (Gregory, Moreno & Brown, 1970; Childs, 1970). The very strong hydrogen bonding found in the crystal structure of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ (Dickens, Prince, Schroeder & Brown, 1972) suggests that complexes involving more than one

PO_4 ion may sometimes be present in solution. However, discrete ion complexes involving Ca and/or PO_4 or AsO_4 in the presence of water molecules have not yet been found in the solid state.

Optical and unit-cell data of seven of the eight possible combinations of (Ca, Mg) (K, NH_4) (PO_4 , AsO_4) $\cdot n\text{H}_2\text{O}$, where $n = 6, 7$ or 8 depending on the combination, are given in Table 5. (We have prepared the eighth combination, $\text{CaKPO}_4 \cdot n\text{H}_2\text{O}$, but it was very unstable.) The four magnesium salts appear to be isostructural in that they all have the space group $Pm2_1n$, their unit-cell dimensions are nearly the same, and they all have six waters of hydration. The structural type is illustrated in Fig. 2, which is the crystal structure of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, struvite (Whitaker & Jeffrey, 1970*a, b*).

The two calcium–ammonium salts, $\text{CaNH}_4\text{PO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{CaNH}_4\text{AsO}_4 \cdot 7\text{H}_2\text{O}$, have slightly larger unit cells than the magnesium salts (particularly in the length of b), but their Weissenberg patterns clearly reveal that they are structurally related to struvite. The increase in cell volume is associated with the greater size of the divalent cation and the presence of the seventh water. These salts have a lower symmetry space group, $P2_1$, but it should be noted that the twofold screw axis is also present in the four magnesium salts. X-ray reflections of the two calcium salts tend to be weak when $h+k=2n+1$, suggesting pseudo-centering on the C face. This corresponds to the actual centering in $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ and the pseudo-centering on the C face apparent in the structure of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (Fig. 2). The presence of the eighth molecule of water in $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ results in a significant increase in the length of c and slight decreases in a and b , as compared to the other two calcium salts; it also allows the space-group symmetry to increase to $Cm2m$ and makes it possible for each of the AsO_4 oxygen atoms to be the acceptor in four hydrogen bonds. It should also be noted that the n glide operation in $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ simulates the C centering operation in $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$.

Some crystallographic properties for $\text{MgKAsO}_4 \cdot 5\text{H}_2\text{O}$ (TVA, unpublished data), $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$ (Lehr *et al.*, 1967) are given in Table 6. Systematic weaknesses in the X-ray reflections of $\text{MgKAsO}_4 \cdot 5\text{H}_2\text{O}$ suggest that it has a pseudo-cell a third the size of its real cell. This pseudo-cell closely resembles the pseudo-hexagonal cell of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, described by Whitaker & Jeffrey (1970*a*), which corresponds to the primitive cell of $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$. The pseudo-cells of $\text{MgKAsO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ are compared in the following tabulation:

	$\text{MgKAsO}_4 \cdot 5\text{H}_2\text{O}$ pseudo-cell	$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ pseudo-cell
a'	6.3 Å	6.941 Å
b'	6.3	6.588
c'	12.39	12.274/2
	120°	121.8°

It is plausible, therefore, that $\text{MgKAsO}_4 \cdot 5\text{H}_2\text{O}$ has the basic struvite structure. Octahedral coordination of the magnesium atom by six independent water molecules is no longer possible and it may be necessary to involve an AsO_4 oxygen atom in the magnesium coordination.

From a comparison of the formulae, $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ (Table 6) is related in composition to $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, struvite, and $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$, the mineral phosphoroesslerite (Table 6). The unit-cell dimensions of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ clearly resemble those of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, the greater length of b (12.29 as compared to 11.10 Å for $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$) possibly reflecting the presence of more waters of hydration in the same way as for the salts in Table 5. The cell dimensions of $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$

are simply related to those of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, but the space group of this compound contains additional symmetry elements ($\bar{1}$ and A) so that a structural relationship to the other two salts in Table 6 is not readily apparent. If the formula is written $\text{Mg}(\text{H}_3\text{O})\text{PO}_4 \cdot 6\text{H}_2\text{O}$, the chemical relationship to $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ is obvious.

It is apparent that the relationships among these compounds are in some instances quite complex and depend on the details of the coordination of the cations and the hydrogen bonding of the water molecules. For example, the two structures, $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, differ considerably in detail. Each of the Ca and K ions in $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ has a coordination polyhedron of eight water molecules; the Mg ion in $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ is coordinated to only

Table 5. *Some compounds with the 'struvite-type' structure*

	$\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$	$\text{CaNH}_4\text{PO}_4 \cdot 7\text{H}_2\text{O}^*$	$\text{CaNH}_4\text{AsO}_4 \cdot 7\text{H}_2\text{O}^\dagger$	$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}^\ddagger$	$\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$	$\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$	$\text{MgKAsO}_4 \cdot 6\text{H}_2\text{O}$
Unit-cell dimensions, Å							
a	7.146 (1)	7.18	7.27	6.941 (2)	7.00	6.91	7.03
b	11.696 (2)	11.96	12.07	11.199 (4)	11.14	11.10	11.26
c	7.100 (2)	6.30	6.38	6.137 (2)	6.14	6.21	6.23
Angle β	90°	90.83°	91.47°	90°	90°	90°	90°
Unit-cell volume, Å ³	593.4	541	560	477.0	479	476	493
Space group	$Cm2m$	$P2_1$	$P2_1$	$Pm2_1n$	$Pm2_1n$	$Pm2_1n$	$Pm2_1n$
Z , formula weights per unit cell	2	2	2	2	2	2	2
Density, calculated, g.cm ⁻³							
X-ray	2.027	1.70	1.91	1.71	1.99	1.85	2.08
Optical	2.10	1.71	1.86	1.71	1.95	1.91	2.15
Crystal morphology	mm	2	2	mm	mm	mm	mm
Refractive indices: N_x	1.497	1.495	1.514	1.496	1.518 ₄	1.477	1.503
N_y	1.516	1.497 ₅	1.516	1.497 ₃	1.519	1.481	1.509
N_z	1.519	1.514	1.535	1.505	1.528	1.487	1.509 ₄
Optic sign	(-)	(+)	(+)	(+)	(+)	(+)	(-)
Optic angle $2V^\circ$: measured	46-47	41.5	34	41	25	-	22.5
calculated	43	43	36	45	29	79	29
Dispersion	$r > v$ moderate	none	none	$r > v$ weak	none	$r > v$ weak	$r > v$ moderate
Optic axial plane	(100)	~(001)	~(001)	(010)	(001)	(001)	(001)
Extinction angle $z\Delta\alpha$ (in obtuse beta)	-	6°	6.5°	-	-	-	-
Orientation: N_x	b	b	b	a	b	b	b
N_y	a	~ a	~ a	b	a	a	a
N_z	c	~ c	~ c	c	c	c	c

* Lehr *et al.*, (1967).

† TVA, unpublished work.

‡ Whitaker & Jeffrey (1970a).

Table 6. *Other probable members of the struvite series*

	$\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}^*$	$\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}^\dagger$	$\text{MgKAsO}_4 \cdot 5\text{H}_2\text{O}^\ddagger$
a	6.55 Å	11.35 Å	10.79 Å
b	12.29	25.36	10.79
c	6.30	6.60	12.39
α	95.3°	90°	90°
β	89.7	95	90
γ	93.6	90	120
Z	1	8	6
Crystal system	triclinic	monoclinic	hexagonal
Space group	$P1$ or $P\bar{1}$	$A2/a$	$P\bar{3}c1$ or $P3c1$

* Lehr *et al.* (1967).

† Hägele & Machatschki (1939).

‡ TVA, unpublished work.

six water molecules, and the NH_4 ion is coordinated to five water oxygen atoms and one PO_4 oxygen atom. The Ca and K ions share a square configuration of water oxygen atoms; the Mg and NH_4 ions share a triangular configuration. Each of the AsO_4 oxygen atoms in $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ is the acceptor in four hydrogen bonds; each of the PO_4 oxygen atoms in $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ is the acceptor in only three hydrogen bonds. The PO_4 group is positioned so that the NH_4 ion hydrogen bonds to O(1) of the PO_4 group (Whitaker & Jeffrey, 1970*a, b*) and to water oxygen atoms. In $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$, the AsO_4 group (in a special position at the intersection of two mirror planes) cannot have the orientation PO_4 has in $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, and its orientation is such that the oxygen atoms are not near the K ion.

$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ exists as the biomineral struvite and has been found (Cohen & Ribbe, 1966; Whitaker, 1968) in excreta from various forms of life, in human lungs (Porter, 1924), in human urinary calculi (Lonsdale & Sutor, 1966) and rat urinary calculi (Rottschaeffer, Sax, Pletcher & Braude, 1970) and in canned goods such as lobster (Ayres, 1942) and salmon (Whitaker & Jeffrey, 1970*a*). After removal from the environment in which it is formed, struvite changes (Whitaker, 1968) into $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, newberyite (Sutor, 1967).

$\text{CaNH}_4\text{PO}_4 \cdot 7\text{H}_2\text{O}$, the calcium analogue of struvite, is very unstable and decomposes to $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, the major inorganic phase in the body, within minutes at

room temperature, even in an aqueous environment. ($\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ was studied here because it was one of the more stable members of the series.) Because of its instability, $\text{CaNH}_4\text{PO}_4 \cdot 7\text{H}_2\text{O}$ probably does not exist as a biomineral, since it would then have to be stable at 37°C . The high hydration of the ions in $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ and its fairly high rate of growth (of the order of $1 \text{ mm} \cdot \text{h}^{-1}$) during its preparation near 0°C suggest that these salts are easily produced in an aqueous environment under favorable conditions. It is conceivable therefore that $\text{CaNH}_4\text{PO}_4 \cdot 7\text{H}_2\text{O}$ exists transiently even at 37°C as a highly hydrated nucleus important in the early stages of crystallization of biominerals.

The structural relationships discussed above speak for the stability of the struvite-type structure and for the importance of the concept of structural types in general. ('Struvite-type' is used here in the sense that the structures show overall similarities, even though they differ greatly in their fine details.) Thus the unusual chemistry of Ca and K ions completely surrounded by water molecules in $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ becomes less surprising when placed in the context of the other compounds in Table 5. The struvite-type structure is the fifth major structural type to emerge in calcium phosphates and related compounds. The five types are:

(i) $\text{M}_5(\text{XO}_4)_3\text{Y}$, the apatite type, of which there are many examples (over 70 are listed in Wyckoff, 1965); $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ (Brown, 1962; Brown, Smith, Lehr & Frazier, 1962) and $\text{Ca}_4\text{O}(\text{PO}_4)_2$ (Dickens,

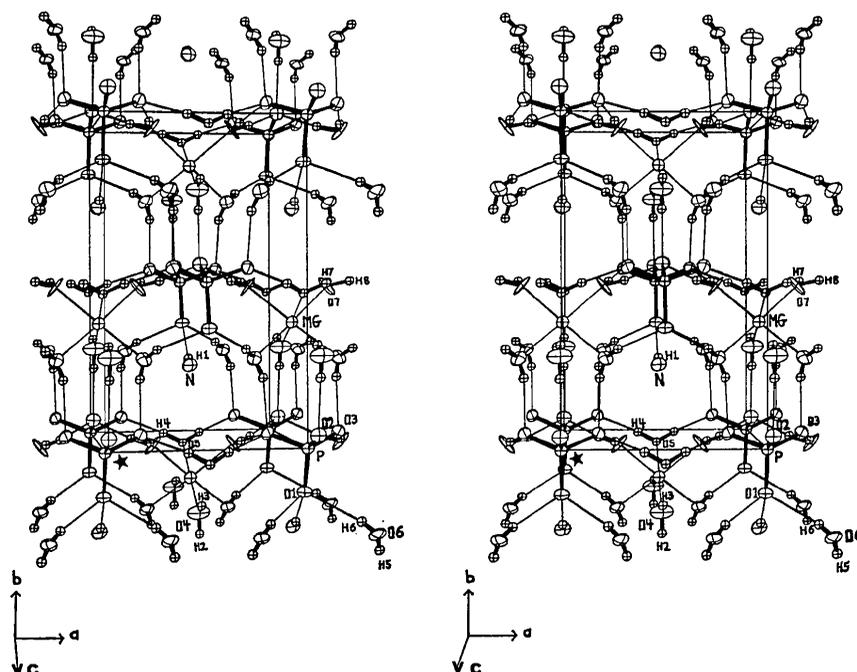


Fig. 2. The crystal structure of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ in an orientation similar to that of $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ in Fig. 1. The atomic parameters for $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ were taken from Whitaker & Jeffrey (1970*a*) with the exception of the thermal parameters of O(5), which were non-positive definite as given. O(5) is designated here by a sphere. The b and c axes of Whitaker & Jeffrey have been interchanged to conform to those of $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ in Fig. 1. The star is at the origin of the coordinate system chosen by Whitaker & Jeffrey.

Kruger, Stewart & Brown, 1972) contain apatite-like layers;

(ii) MXO_4 -sheet containing compounds:

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Atoji & Rundle, 1958), $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (Beever, 1958; Jones & Smith, 1962; Curry & Jones, 1970), $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (Smith, Lehr & Brown, 1955; MacLennan & Beever, 1956; Jones & Cruickshank, 1961; Dickens & Bowen, 1971*b*), CaHPO_4 (MacLennan & Beever, 1955; Jones & Cruickshank, 1961; Dickens, Bowen & Brown, 1972), and probably $\text{Ca}_2\text{NH}_4\text{H}_7(\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$, $\text{Ca}_2\text{KH}_7(\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$ and $\text{CaClH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (Brown, Smith, Lehr & Frazier, 1958) contain corrugated sheets; $\text{Ca}_2\text{PO}_4\text{Cl}$ (Greenblatt, Banks & Post, 1967; 1969) contains planar sheets;

(iii) $(\text{M}, \text{N}, \square)_4(\text{XO}_4)_2$ or glaserite-type after $\text{K}_3\text{Na}(\text{SO}_4)_2$ (glaserite): $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$ (Dickens & Brown, 1971*a*) and $\text{Ca}_7\text{Mg}_9(\text{Ca}, \text{Mg})_2(\text{PO}_4)_{12}$ (Dickens & Brown, 1971*b*) both have structures related to the glaserite structure, but with systematic cation vacancies, denoted \square in the general formula above; $\alpha\text{-Ca}_3(\text{PO}_4)_2$ (Ando, 1958; Dickens & Brown, 1971*b*), CaNaPO_4 and $\text{Ca}_4\text{Na}_2(\text{PO}_4)_4$ (Ando & Matsuno, 1968), and the high temperature solid solution between $\alpha\text{-Ca}_2\text{SiO}_4$ and $\bar{\alpha}\text{-Ca}_3(\text{PO}_4)_2$ (Berak & Wojciechowska, 1956; Nurse, Welch & Gutt, 1959; Dickens & Brown, 1971*a*) may be other examples of glaserite-type structures with systematic cation vacancies; $\text{CaK}_3\text{H}(\text{PO}_4)_2$ (Brown & Fowler, 1967) is probably a monoclinic distortion of the $\text{K}_3\text{Na}(\text{SO}_4)_2$ structure.

(iv) $\text{M}_3(\text{XO}_4)_2$. Compounds with large cations such as $\text{Ba}_3(\text{PO}_4)_2$ and $\text{Sr}_3(\text{PO}_4)_2$ (Zachariassen, 1948) and $\text{Ba}_3(\text{VO}_4)_2$ (Susse & Buerger, 1970) have high symmetry and a small asymmetric unit. $\text{Ca}_3(\text{AsO}_4)_2$ (Gopal & Calvo, 1971) and $\beta\text{-Ca}_3(\text{PO}_4)_2$ formed at $\sim 1000^\circ$, or $\sim 1350^\circ$ with Mg^{2+} as impurity (Dickens, Bowen & Brown, 1971) crystallize in distorted versions of the $\text{Ba}_3(\text{PO}_4)_2$ structure. Synthetic whitlockite, grown hydrothermally, $(\text{Ca}, \text{Mg})_{20}\text{H}_2(\text{PO}_4)_{14}$, has an even more distorted version of this structural type (Calvo & Ito, 1972).

(v) $\text{M}^{2+}\text{N}^+\text{XO}_4 \cdot n\text{H}_2\text{O}$, or struvite-type after $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (struvite), where n is 6 to 8 and N is a larger cation than M . Several compounds which probably have the struvite-type structures are given in Tables 5 and 6.

Most of the optical and X-ray data on arsenates in Table 5 have not been previously reported. The optical data were obtained by James R. Lehr and A. William Frazier and the X-ray data by James P. Smith in association with one of the authors (W. E. Brown). We are indebted to the Tennessee Valley Authority for permission to publish those results. B. M. Wallace grew the crystals used in this study; J. S. Bowen and P. B. Kingsbury provided technical help; and C. K. Johnson's ORTEP program was used in drawing the figures. We thank A. Whitaker and J. W. Jeffrey for copies of their papers prior to their publication. This

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The Crystal Structures of Free Radical Salts and Complexes. IV. (1,1'-Ethylene-2,2'-bipyridylum)²⁺-(7,7,8,8-Tetracyanoquinodimethane⁻)₂

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Crystals of (C₁₂H₁₂N₂)²⁺(C₁₂H₄N₄)₂⁻ are triclinic, space group *P* $\bar{1}$, with lattice constants $a=7.416$, $b=13.371$, $c=14.625$ Å, $\alpha=87.800^\circ$, $\beta=95.567^\circ$, $\gamma=95.200^\circ$, $Z=2$. The structure was solved by Patterson methods and refined by block-diagonal least-squares analysis using 4785 observed reflexions measured on a Hilger and Watts computer-controlled, four-circle diffractometer. The structure contains columns of tetracyanoquinodimethane (TCNQ) ions packed in a plane-to-plane manner. The four TCNQ ions per unit cell form two crystallographically independent centrosymmetric dimers. Within the dimers there are short interplanar spacings of 3.22 and 3.26 Å between the TCNQ ions indicating charge-transfer interaction. Between the dimers there is a gap of 3.59 Å.

Introduction

Molecular complexes containing ions and molecules of 7,7,8,8-tetracyanoquinodimethane (TCNQ) include some of the best electrically conducting organic compounds known. As a part of a series of crystal structure determinations of TCNQ complexes to elucidate the relationship between their structures and electrical properties, the crystal structure of (1,1'-ethylene-2,2'-bipyridylum)²⁺ (TCNQ⁻)₂ is reported.

Experimental

Crystal data

(C₁₂H₁₂N₂) (C₁₂H₄N₄)₂, M.W. 592.6,
Triclinic,
 $a=7.416 \pm 0.001$, $b=13.371 \pm 0.001$,
 $c=14.625 \pm 0.001$ Å,

$\alpha=87.800 \pm 0.004^\circ$, $\beta=95.567 \pm 0.004^\circ$,
 $\gamma=95.200 \pm 0.005^\circ$,
 $U=1436.8$ Å³;
 $D_m=1.36$ g.cm⁻³, $Z=2$, $D_c=1.37$ g.cm⁻³,
 $F(000)=612$.
Mo *K*α ($\lambda=0.7107$ Å), $\mu=0.94$ cm⁻¹.
Space group *P* $\bar{1}$ (assumed).

Purple lath-shaped crystals of the complex salt were obtained when 1 mole of 1,1'-ethylene-2,2'-bipyridylum bromide (diquat bromide) and 2 moles of LiTCNQ were dissolved in hot acetonitrile and added to an excess boiling solution of LiTCNQ in acetonitrile and allowed to cool slowly to room temperature. The space group and the unit-cell dimensions were obtained initially from oscillation and Weissenberg photographs taken with the crystals rotating about all the three crystallographic axes using Cu *K*α radiation. The