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The Crystal Structure of CaKAsO₄.8H₂O

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CaKAsO₄.8H₂O 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[CaKAsO₄.8H₂O]. 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 CaKAsO₄.8H₂O are completely hydrated. Ca coordinates to eight water oxygen atoms with Ca···O distances in the range 2.460 (5) to 2.490 (3) Å. K coordinates to eight water oxygen atoms with K···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 AsO₄ 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 AsO₄^{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 CaKAsO₄.8H₂O is related to that of MgNH₄PO₄.6H₂O, 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 CaCO₃.6H₂O (Dickens & Brown, 1970) that in the crystal structure, the Ca²⁺ and CO₃²⁻ ions are all in [Ca²⁺, CO₃²⁻]° ion pairs which are completely surrounded 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 CaKAsO₄.8H₂O.

Data collection and structure refinement

CaKAsO₄.8H₂O was prepared by mixing 20 cm³ of $0.1 M.1^{-1}$ CaCl₂ solution, 25 cm³ $1.0 M.1^{-1}$ tripotassium citrate solution and 10 cm³ $3.0 M.1^{-1}$ KOH solution at 0°C and then adding 10 cm³ $0.2 M.1^{-1}$

 K_2 HAsO₄ solution. The resultant mixture was kept at 0°C; precipitation of CaKAsO₄.8H₂O began after about two hours. This procedure is an adaptation of that given for CaNH₄PO₄.7H₂O by Lehr, Brown, Frazier, Smith & Thrasher (1967).

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

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

Formula (ideal): CaKAsO₄.8H₂O. Cell at 25 °C: orthorhombic. a = 7.146 (1) Å b = 11.696 (2) c = 7.100 (2) Volume = 593.4 Å³.

Space-group $Cm2m(C_{2\nu}^{14})$; 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 (1971*a*, *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 $\mu(Mo) = 39.6 \text{ cm}^{-1}$. The maximum and minimum transmission factors were 0.83 and 0.66 respectively. 2163 reflections were collected from the *hk1* and *ħk1* 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 Crystallogra-phy* (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 $\sum w(F_o - 1)^{10}$

 $F_c)^2$. 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 \cdots 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 \cdots 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 electrondensity 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 $\left[-\frac{1}{4}(a^{*2}B_{11}h^2 + b^{*2}B_{22}k^2 + c^{*2}B_{33}l^2 + 2a^*b^*B_{12}hk + 2a^*c^*B_{13}hl + 2b^*c^*B_{23}kl\right]$.

	x	у	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) <i>l</i>	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: $x, y, z; -x, y, z; -x, y, -z; x, y, -z; \frac{1}{2} + x, \frac{1}{2} + y, z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2$

Table 2. Observed and calculated structure factors for CaKAsO₄.8H₂O

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

H.O.O	9 227 232 9 11 229 221 980	10 103 97 0	4.4.0	4.5.4	2 327 321 67 8 169 181 958 4 309 302 62 10 88 99 47	H,9,7	4+11+2	H+12+10	4 77 101 41 H+17+2
2 795 734 0 1470 1456 U 5 755 765 U	H+1+4	4+2+8 0 251 276 916	01161 1013 990 2 143 115 124 4 500 455 5	1 237 239 968 3 307 314 971	6 221 214 75 8 212 211 67 H+8+2	1 261 275 95B 3 345 352 927	1 323 325 52 3 297 303 31	n 124 114 48 2 40* 49 24	H:14:9 1 120 124 997 3 79 81 4
9 463 479 D 10 444 446 D	1 191 191 27 3 45 53 766	2 102 114 700 4 192 199 924	6 155 162 903 8 157 154 993	7 189 194 959 9 138 147 984	HIDIO 0 303 294 987	5 148 164 982 7 263 263 929 9 110 108 947	5 274 249 71 7 199 204 22	4+13+0	0 141 143 984 5 119 124 995 2 153 152 929 7 64 43 36
HIQ.1	5 224 234 33 7 40 38 851 9 116 100 45	6 129 134 889 8 85 92 940	10 127 125 921 12 36• 35 950	11 71 79 930	0 161 160 929 4 512 296 987 2 215 212 884 6 239 232 28	H.9,8	4+11+3	1 445 410 945 3 402 492 957	H.15.0 H.17.3
n 86 31 500	11 39• 44 961	4,2,9	H+4+1	1 202 215 68	4 164 157 910 8 217 230 10 6 143 136 898 10 99 113 995 8 129 123 889	1 201 214 126	1 269 283 999	5 343 312 936 7 282 274 952	1 138 136 39 1 223 217 969 3 68 72 157 3 268 251 962
2 194 193 U 4 40 21 500	H+1+5	0 341 338 24	0 443 431 35 21179 1133 59	3 297 302 109 5 120 131 997	H+6+3	5 182 1A3 128 7 114 120 130	5 253 248 8 7 133 132 970	4.13.1	7 374 41 231 7 199 186 983 9 102 97 13
A 28+ U 0 10 59 57 U	3 500 501 55 5 921 449 968	2 247 241 46 4 266 264 34 6 215 213 28	4 508 509 56 6 493 481 39	7 210 213 102 9 104 95 34	0 152 160 103 2 363 380 108 2 363 359 967	H.9.9	9 113 109 990	1 173 181 121	H+15+1 H+17+4
12 33+ 15 0	7 533 343 45 9 208 218 983	8 162 141 60	10 219 217 31	11 88 87 83	4 154 159 95 6 235 231 36 6 135 130 112 4 158 162 973	1 165 179 908	H+11+4	3 137 149 163 5 149 152 113	1 55 62 50
HI012	11 200 197 6	4.2.10	H+4+2	1 300 297 964	10 124 115 81	5 156 155 920 7 105 115 900	3 115 127 46 5 273 273 11	9 82 86 159	5 220 212 989 7 204 204 6 H,17,5
2 633 667 0 4 556 581 0	1 271 270 992	2 142 132 5	n 726 7ng 214 2 265 265 951	3 289 286 9 5 255 259 939 7 161 162 5	H,B,4 0 105 106 248	11.9.10	7 73 84 55 9 160 150 16	4+13+2	9 142 136 7 1 154 167 4
6 468 473 0 6 332 331 U	3 186 162 87 5 265 269 974	6 122 114 960 8 86 87 995	4 307 343 796 6 190 197 808	9 185 170 960 11 58 80 955	4 99 91 801 2 311 303 940 4 377 379 15	1 105 102 96 3 103 86 55	4+11+5	1 415 423 950 3 246 255 949 5 430 411 960	H+15+2 3 131 144 994 5 142 149 4
12 179 178 0	9 131 120 1	4.2.11	4 147 145 941 10 119 129 773	4,5,7	H+6+12 6 225 221 997 4 213 209 976	5 85 93 118	1 210 212 949 3 225 256 920	7 159 160 941 9 234 232 955	3 133 144 27 H.17.6 5 111 69 886
H+0+3	4.1.7	0 104 99 51 2 211 191 58	H1413	1 296 290 21	2 110 119 68	H+9+11	5 127 125 975 7 196 195 924	H+13+3	7 88 91 25 1 68 75 53 3 91 70 72
2 359 355 500 2 107 107 500	1 419 416 995	4 123 106 71 6 135 124 53	1 586 588 4	5 168 167 59 7 248 255 992	H+7+0 0 117 105 899	3 192 188 914	4+11+6	1 109 136 162 3 119 190 139	H,17,7 1 263 270 978
5 270 19 0 4 93 97 500	5 316 323 14 7 262 272 963	4+2+12	4 486 498 13	9 122 112 57	1 418 358 784 2 350 371 996 3 270 233 763 4 134 140 930	H+10+0	1 263 256 21	5 74 108 192 7 93 101 115	3 212 225 988 1 158 153 958 5 243 237 978 3 190 187 978
10 64 27 U 12 54 30 50U	9 173 170 11	0 154 160 917 2 35* 55 823	A 291 306 33 10 214 214 15	1 261 256 948	7 110 105 789 R 147 134 957 9 195 202 853 10 67 62 14	2 528 401 921	3 205 214 16 5 245 217 27 7 159 160 16	9 67 74 220	7 145 157 968 H+18+0
H+0+4	Halas	4 104 103 915	12 165 155 25	3 237 240 968 5 202 207 933	11 59 66 782 4+8+6	6 380 356 911 8 278 269 908	9 122 133 28	1 333 331 937	0 144 140 912
01541 1505 0 2 500 552 U	3 59 16 113 5 101 116 964	11129 969 61	0 525 517 942	9 152 147 949	H:7:1 0 218 238 984	10 216 204 891	H.11.7	5 279 268 933	3 53 53 97 4 121 116 942 5 114 115 974 6 41* 67 986
- 532 560 U	7 32• 15 194 9 63 56 997	31029 972 156 5 699 713 995	2 105 117 885	4+5+9	3 632 574 47 4 227 214 983 5 334 335 141 6 150 160 995	0 415 420 137	3 104 114 982 5 103 186 996	9 180 167 940	7 348 24 139 H+18+1
10 350 350 U 12 165 165 0	H.1.9	9 371 366 31	R 133 133 967	1 131 127 46 3 166 161 97 5 92 85 999	7 366 362 49 a 156 164 983 9 197 193 106 10 99 96 987	2 312 312 64 4 300 296 128	7 67 82 973	4,13,5	1 193 218 11 2 195 199 20
H+P+5	1 257 263 979 3 222 227 29	4+3+1	17 58 40 941	7 127 118 103	H.7.2 H.R.7	6 291 276 103 R 133 139 91	4,11,8	1 166 155 103	3 234 255 20 4 142 146 36 5 154 147 5 6 124 137 39
U 97 91 U	5 225 228 948 7 185 171 30 7 116 126 960	1 285 295 218	4+4+5	H+5+10	0 221 219 98 1 509 509 931 2 177 183 945	H,10.2	3 11A 123 62 5 159 155 55	7 79 72 182	H+15+6
* 75 68 U 5 183 194 U	H+1+10	5 194 203 753 7 140 149 901	2 798 A15 62 4 356 360 54	3 145 141 983 5 105 103 971	3 511 525 913 4 154 152 55 5 248 252 945 6 128 130 36 7 341 350 908 4 83 04 054	0 459 450 3	7 74 91 59	H+13+K	0 78 76 999
3 70 61 U 10 60 55 0	1 137 134 43	9 55 72 778 11 100 92 846	4 312 401 47 4 319 321 61	7 105 100 974	9 184 185 922 11 119 118 893 Helles	4 344 337 960 6 242 238 911	1 86 89 936	3 242 236 958 5 308 292 952	5 74 69 958 6 85 77 915
H+0+6	5 143 129 43 7 39+ 50 64	4,3,2	10 157 164 34 H+4+6	N-5-11	H.7.3 U 280 265 26	A 159 146 888 10 147 147 949	3 119 118 913 5 444 48 970	7 147 160 951	H+15+7 H+18+3
2 481 474 U	H+1+11	11136 1153 19 3 873 879 11	0 170 193 831	3 157 146 32 5 98 75 112	1 627 636 71 4 247 232 14 3 607 613 64 6 168 173 20	H+10+3	4+11+10	H+13+7	1 185 196 991 0 140 166 990 3 146 150 999 2 194 188 35 5 185 182 980 5 182 150 897
1 288 296 U	1 260 236 994	5 699 700 29 7 462 471 15 9 399 383 40	2 102 105 984	H+5+12	5 396 408 79 4 164 160 999 7 380 387 69	0 296 301 174 ° 2 354 378 128	1 163 154 4 3 105 112 10	3 97 117 119 5 42* 80 203	6 137 135 29 H+15+8
10 242 242 0	5 201 141 3	11 212 220 12	A 92 A3 992 10 62 65 811	1 163 151 941 3 143 132 972	11 187 192 82 0 37• 69 970	4 249 230 160 6 259 274 134 8 146 145 139	H+12+0	7 91 90 94	H-18-9 1 80 58 918
975 64 U	1 77 58	4,3,3	4.4.7	*** 6 • 0	H+7+4 2 212 197 18 4 108 85 979	10 147 150 150	0 459 435 77 2 161 154 982	1 178 196 935	2 116 94 18 H=15+9 4 103 110 944
2 159 152 500	3 86 43 151	3 193 203 897 5 347 375 794	0 3AA 377 15 2 322 320 13	0 476 450 71 21077 950 101	3 222 214 866 5 250 263 864 dist 10	H.10.4	4 321 301 71 6 165 167 44	3 149 154 943 5 191 192 933	1 130 132 2 H+18+5
6 31* 9 500 8 76 71 500 10 38* 25 u	4,2,0 0 978 776 943	7 124 141 919 9 131 143 794	4 297 309 21 6 240 297 11	4 525 484 71 5 423 400 101	7 133 118 852 9 164 169 872 U 169 169 9	2 341 357 923 4 346 363 907	10 121 120 64	4.13.9	H+16+0 0 115 135 106 2 172 166 13
rl+0+8	2 962 916 69	4,3,4	10 158 155 11	10 164 161 84	11 38* 61 829 2 134 131 945 4 150 147 990	6 264 277 914 9 195 212 911	4+12+1	1 74 75 112 3 67 55 213	0 341 343 29 4 122 123 74 2 338 336 985
0 459 481 U	6 351 350 994 6 257 255 33	1 666 667 32	H.4.9	7+6+1	1 280 292 131 H.S.11	H+10+5	2 399 404 950	4,13,10	9 325 314 18 H,18,6 6 232 232 993 8 244 217 9 0 70 58 048
4 385 360 0 5 273 281 0	12 109 113 14	5 507 535 999 7 345 354 99	2 125 134 915 4 164 165 899	0 360 336 755 2 611 557 891	3 350 351 30 5 224 233 190 0 74 58 90 7 254 262 33 0 71 71 000	0 356 380 119	6 316 120 962 8 212 199 943	1 175 1R0 999	2 77 82 935 H+10+1
-1 193 195 0 10 198 185 0	H+2+1	9 202 311 27 11 180 174 52	6 96 110 865 8 90 99 941	4 310 293 837 6 258 250 872	9 126 133 140 4 61 44 17 11 123 129 76	4 254 251 104 5 210 215 91	4,12,2	0 325 298 968	H+19+0 0 33* 27 6 2 AU AB 120 1 200 105 42
11.7.9	2 910 920 52	4.3.5	4,4.0	8 217 232 873 10 116 116 847 12 122 119 878	H+9.0 H+7+6	8 123 114 54 10 145 150 117	0 138 138 22	2 272 273 111 4 256 235 15	4 52 36 78 3 157 151 24 6 54 44 99 5 172 183 47
2 160 151 U	6 496 491 16 4 281 290 50 10 235 282 11	1 40 56 793	0 203 209 1 2 429 413 42	H+6+2	1 244 252 888 3 252 245 25 3 286 290 888 5 293 242 177	H+10+6	4 99 110 109 6 86 99 145	9 162 157 92	8 38* 39 111 H+19+1 H+16+2
6 98 86 0 -, 48 31 0	12 150 147 44	7 120 124 883	6 24A 242 25 A 24A 242 25	0 941 885 84 2 410 397 70	5 164 170 885 7 177 179 43 7 177 181 880 9 144 132 139 9 124 127 889 11 04 01 110	0 307 322 940 2 275 280 862	8 A2 100 199 10 77 52 57	H+14+1	0 312 329 928 3 84 67 892
2+0.16	H,2,2	11 63 70 847	4+4+19	4 664 634 75 6 342 330 83	H17.7 H19.1	6 192 205 898 8 160 168 895	4,12,3	2 281 280 975 9 238 233 975	2 252 254 18 5 354 26 807 4 272 272 954 6 183 105 968 M-10-1
11 425 418 U 2 250 255 U	2 595 583 45	1 594 591 44	n inu ay yri 2 369 30 48	8 319 319 68 10 235 208 85 12 131 139 86	1 390 394 59 1 455 434 905	4.10.7	0 322 318 1 2 273 297 920	6 225 216 967 R 140 142 970	8 175 176 2 1 210 224 20
4 325 324 U 1, 232 241 0	6 155 168 832 9 65 71 927	3 517 523 57 5 455 462 33	8 83 91 789 6 37• 30 927	H+6+3	5 284 292 53 5 341 295 921 7 260 263 71 7 312 309 896	0 136 161 156 2 260 257 131	4 251 243 975 6 252 243 958 8 139 151 933	4+14+2	H+16+3 3 250 256 27 5 166 158 9
H+0+11	12 33+ 31 637	9 235 280 46	4+4+11	0 389 387 228	9 161 177 49 0 170 176 893 11 146 156 930	4 144 149 154 6 182 185 133	10 146 150 992	n 170 192 84 2 56 68 977	2 64 59 931 H+19+3 4 57 15 84
0 444 52 0	H1213	4.3.7	2 168 166 37	4 293 315 816 6 264 277 888	1 185 192 913	H 101 109 136	H,12,4	4 145 145 77 6 70 71 15 8 92 93 93	6 48 24 955 1 81 74 932 3 90 79 896
- 37+ 21 U	2 651 662 22	1 231 247 842	6 137 133 28	8 229 232 889 10 105 123 829 12 127 125 805	3 187 198 908 1 523 541 95 5 143 146 910 3 356 370 127	0 535 535 953	2 98 100 34 4 204 208 82	4.14.3	N.19.4 D 287 290 4
4.0.12	6 362 372 991 8 219 224 37	5 229 250 A13 7 98 88 944	4.4.1>	H+6+4	9 130 105 909 7 214 232 148	2 174 180 904 4 195 149 939 5 130 147 925	6 115 117 54 8 71 84 89	2 251 238 203	2 280 287 983 1 164 183 39 4 250 264 1 3 153 156 25
3 138 177 0 > 172 157 U	12 136 132 33	9 109 112 814	n 44 71 d09 2 40+ 56 949	0 441, 440 71	H17.9 11 124 135 141	* 105 119 917	4,12,5	6 165 165 991 6 163 165 948	6 144 202 483 H+19+5 H+16+5
€ 163 151 U	***5.4	1 372 366 17	4.5.0	6 339 337 85	3 243 226 40 5 149 150 160 1 394 400 955	H+10+9	0 377 382 932 2 347 363 981	A 110 105 954	0 38* 46 958
H+1+0 1 146 392 99	2 344 387 28 4 356 378 967	3 335 325 44 5 298 308 6 7 224 215 46	1 114 119 169 3 302 241 953	8 329 336 77 10 173 157 79	7 175 174 34 3 493 495 921 5 251 229 984	2 133 133 45	6 277 287 966 8 178 185 956	0 229 231 975	2 104 115 159 H+20+0 4 35* 45 44 6 34* 55 115 0 35* 34 134
3 138 165 198 5 395 395 69	5 228 243 955 8 101 181 10	9 200 197 26	7 214 206 960	H+6+5	1 94 109 849 11 159 163 850	6 138 140 93	4+12+6	2 184 190 104 9 194 192 17	2 108 95 A94 H+16+6 4 49 36 7
7 72 87 865 9 151 145 71	10 123 140 925 12 86 86 989	H+3+9	11 63 69 924	0 208 204 911 2 333 336 860	3 85 97 846 5 100 95 844 H.9,4	0 189 185 896	0 154 160 34 2 95 110 152	R 131 173 88	0 215 227 970 H+20+1
H+1+1	4.2.5	3 100 102 A51 5 44 44 223	1 371 362 41	4 218 218 880 6 171 184 876 8 175 175 867	H.7.11 1 259 259 129	2 164 161 847 4 165 159 891	4 122 122 73 6 84 85 90	H+14+5	4 207 201 987 0 163 163 19 2 170 173 13
1 939 976 b	11 761 769 26 2 526 532 59	7 95 67 947 9 34• 23 760	3 605 576 50 5 206 200 10	10 80 92 875	1 177 172 54 5 245 240 160 3 180 170 55 7 145 157 78	d+10+11	8 59 71 132	0 256 256 9 2 260 255 955 9 215 213 997	H/16/7 4 136 144 11
596 608 986 7 433 433 23	6 398 409 30 8 246 251 61	H.3.10	0 147 146 33 11 132 128 39	U 391 389 85	9 149 136 52 4 132 131 132 11 96 91 132 H+7+12	0 101 88 102 2 129 120 95	0 213 218 17	6 210 193 970 8 135 134 968	2 55 43 871 4 38* 14 205 0 72 97 926
) 265 266 U 11 240 244 999	N.2.4	1 292 282 53	H+5+2	2 309 311 95 4 328 345 85	1 89 94 918 41915	H+11+0	2 144 197 917 4 161 170 995 6 160 186 967	H+14+6	2 37+ 43 34 H+16+8
11.1.2	n 407 404 954	7 169 182 90	1 743 728 939	6 223 220 104 8 218 220 81 10 137 134 04	H+8+0 1 322 335 885 3 294 298 859	1 390 339 998 1 132 123 1	8 116 109 940	n 153 163 57 2 107 115 78	0 175 189 958 2 185 176 983 0 142 157 53
1 432 514 897	2 M9 69 19 4 252 245 972	H+3+11	5 528 555 919 7 247 247 22	H+6+7	0 727 644 43 7 201 204 877 2 443 379 872 7 156 162 877	5 408 357 989 7 76 81 48 9 190 185 994	H+12+8 D 103 105 A7	4 151 143 69 6 A2 94 54	2 184 190 994 H+17+0
7 117 95 177	8 81 94 993 10 112 119 934	1 79 94 898 3 74 65 993 5 94 95 847	4 786 247 944 11 124 114 957	2 329 247 752	4 493 441 12 6 269 241 984 HI946 8 239 229 956	11 86 8A 25	2 39 62 176 4 85 81 136	4.14.7	H-20,4 1 53 58 105 3 132 131 87 0 454 40 71
11 66 501000	H,2,7	H+3+12	4+5+3	4 178 197 810 6 160 173 880	10 167 158 15 1 256 272 85	H+11+1	5 39+ 55 110	0 167 163 874 2 111 171 5	5 33* 6 142 7 86 98 100 H+21+0
1 717 754 992	0 111 129 921 2 389 376 34	1 191 182 27 3 192 168 29	1 526 526 5 3 662 666 994 5 234 251 34	8 150 159 889 10 93 90 818	**8*1 5 235 237 80 7 124 133 169	3 283 287 942 5 250 220 994	0 221 215 915	6 129 108 942	**17*1 1 96 90 925
1 556 567 980 5 457 477 7	• 132 134 4 6 206 214 9		7 575 342 996 9 163 164 35	H+6+8	2 534 496 991 4 221 206 993	7 212 209 940 9 98 100 976	2 205 205 987 4 177 177 947	4,14,5	1 216 216 992 H+21+1 3 227 215 992
/ 364 382 980	H 162 147 50		11 135 147 6	0 343 338 64	6 259 250 17	++. 103 401		2 71 78 76	3 183 187 488 1 92 100 42 7 177 156 990

2.39 Å from O(2), 2.30 Å from H(3) and 2.65 Å from K. Thus, because it does not seem to fill all the requirements of any one chemical species, it is attributed to the background.

The structure as refined in space-group Cm2m requires that the chemical formula contain eight water molecules unless there are statistical vacancies in some of the water positions. In the earlier stages of this work we believed that the formula contained seven molecules of water, by analogy with $CaNH_4AsO_4$. 7H₂O. The thermal parameters of the oxygen atoms of the water molecules are fairly close to those of the oxygen atoms in the AsO₄ ion and thus the formula is $CaKAsO_4$.8H₂O with no statistical vacancies. To confirm this, a sample of CaKAsO₄.8H₂O 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 leastsquares 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 $CaKAsO_4.8H_2O$ 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 Ca...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 $O \cdots O$ distance in this polyhedron is 2.789 Å for O(3)...O(4). All other O...O distances are a little over 3 Å. The shortest $Ca \cdots O$ distances are to the approximate square of water oxygen atoms $O(3^i)$, $O(3^{ii})$, $O(4^i)$, $O(4^{ii})$ (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 $Ca \cdots O$ bonds are to those water oxygen atoms in edges common to the coordination polyhedra of Ca^i and K^i . These oxygen atoms, $O(5^i)$ and $O(5^{ii})$, are strongly to Kⁱ, though not as strongly as they are to Caⁱ.

Table 3. Probable positions of the hydrogen atoms in $CaKAsO_4.8H_2O$

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

	Difference synthesis			Least-squares refinements			Calculated		
	x	у	z	x	у	Z	x	у	z
H(1)	0.39	-0.05	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 CaKAsO4.8H2O. 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.

Å

Table 4. Interatomic distances and angles in CaKAsO₄.8H₂O

The cation environment	s	
Ca, O(4 ⁱ , 4 ⁱⁱ) Ca, O(3 ⁱ , 3 ⁱⁱ) Ca, O(5 ⁱ , 5 ⁱⁱ))) , 5 ⁱⁱⁱ , 5 ^{iv})	2·460 (5) Å 2·470 (6) 2·490 (3)
K, O(5 ⁱ , 5 ⁱⁱ , K, O(3 ⁱⁱⁱ , 3 ⁱⁱ K, O(4 ⁱⁱⁱ , 4 ⁱⁱ	5 ^v , 5 ^{vi}) ^v)	2·746 (3) 2·919 (6) 2·960 (7)
The AsO ₄ group and its	environment	
As-O(1,1) As-O(2,2)		1.682 (4) 1.684 (<i>a</i>) 1.690 (<i>b</i>) 1.684 (4) 1.685 (<i>a</i>) 1.692 (<i>b</i>)
O(1)-As-O(2 O(1)-As-O(2 O(2)-As-O(2	1) 2) 2)	113·1 (3)° 107·5 (1) 113·7 (3)
$\begin{array}{c} O(1), O(1)\\ O(1), O(2)\\ O(2), O(2)\\ O(1), H(2^{i}, 2\\ O(1), H(4^{i}, 4\\ O(1), O(5^{ii}, 2\\ O(1), O(4^{iv}, 0\\ O(2), H(1^{i}, 1\\ O(2), H(3^{i}, 3\\ O(2), O(5^{v(1)})\\ O(2), O(3^{v(1)})\\ O(2), O(3^{v$	2111) 2110) 5110) 4110) 1†)†	2.807 (7) 2.715 (5) 2.820 (7) 1.87 1.81 2.759 (4)* 2.830 (4)* 1.89 1.81 2.755 (4)* 2.848 (4)*
The environments of the	a watar molecules	
H(1), O(3), H(1)	$\begin{array}{c} O(3^{iii}), Ca^{ii}\\ O(3^{iii}), K^{i}\\ O(3^{iii}), O(2^{i}, 2)\\ H(1), O(2^{i})\\ O(3) - H(1) - O(2^{i})\\ O(2) - O(2^{i})\\ O(2) - O(2^{i})\\ O(3) - H(1) - O(2^{i})\\ O(3)$	2.469 (6) 2.918 (6) 2.848 (4) 1.89 2) 175.7° 2) 08.8 (2)
H(2), O(4), H(2)	$O(4^{iv}), Ca^{ii}$ $O(4^{iv}), K^{i}$ $O(4^{iv}), O(1, 1)$ H(2), O(1) O(4)— $H(2)$ - $O(1)$	$\begin{array}{c} 2 \cdot 459 & (5) \\ 2 \cdot 459 & (5) \\ 2 \cdot 960 & (7) \\ 2 \cdot 830 & (4) \\ 1 \cdot 87 \\ 1 & 175 \cdot 6^{\circ} \end{array}$
H(3), O(5), H(4)	$\begin{array}{c} O(1), O(4)-O(\\ O(5^{i}), Ca^{i}\\ O(5^{i}), K^{i}\\ O(5^{i}), O(2^{v})\\ O(5^{i}), O(1)\\ H(3), O(2^{v})\\ H(4^{i}), O(1)\\ O(5)-H(3), O(2\\ O(5)-H(4), O(1)\\ O(1), O(5), O(2\\ O(5), O(2)\\ O(5)\\ O(5), O(2)\\ O(5$	$\begin{array}{cccc} 1) & 98.7 & (2) \\ 2.490 & (3) \\ 2.746 & (3) \\ 2.755 & (4)^{\prime} \\ 2.759 & (4)^{\prime} \\ 1.81 \\ 1.81 \\ 1.68.7^{\circ} \\ 1.68.7^{\circ} \\ 1.9.4 & (1) \\ 1.9.4 & (1) \end{array}$

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 variancecovariance 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 $O(2^i)$ on the right hand side of the AsO₄ ion in the center of the figure are combined. O(2) and $O(2^i)$ 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 $O(3^{iii})$, $O(3^{iv})$ and $O(4^{iii})$, $O(4^{iv})$ (see Kⁱ in Fig. 1), which are the closest water oxygen atoms to Caⁱⁱ. The Kⁱ ion instead forms stronger K...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 K...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 \angle 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 $H(4) \cdots H(4')$, 2.102 for $H(1) \cdots$ 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 CaKAsO₄.8H₂O 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 AsO₄ groups are CaHAsO₄ H₂O, haidingerite (Calleri & Ferraris, 1967), 2H₃AsO₄ H₂O (Worzala, 1968), CaHAsO₄. 2H₂O, pharmacolite (Ferraris, 1969), Na₂HAsO₄ 7H₂O (Baur & Khan, 1970) and CaHAsO₄, weilite (Ferraris & Chiari, 1970). The average As–O distance in CaHAsO₄. H₂O, 1.686 Å, is in good agreement with that observed in CaKAsO₄.8H₂O, as are the averages, 1.690 and 1.679 Å, of the two crystallographically different AsO₄ groups in CaHAsO₄. The average value in Na₂HAsO₄. 7H₂O, 1.678 Å, is slightly shorter than the above values. The average value of As-O in the imprecisely determined structure of $2H_3A_5O_4$. H_2O 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 AsO₄ groups in the above compounds differ from that in CaKAsO₄ 8H₂O by cation coordination and covalent bonding of H to the oxygen atoms of the AsO₄ 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 AsO₄ 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 0.01-0.02Å for PO_4^{3-} groups in various structures. Thus the concept of constant average X-O distance in XO₄ groups may not be very useful.

The complete hydration of the Ca and K ions in CaKAsO₄.8H₂O differs from that of another highly hydrated calcium salt, CaCO₃.6H₂O (Dickens & Brown, 1970), where all cations are in [CaCO₃]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 Ca(H₂PO₄)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 AsO₄ 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, NH₄) (PO₄, AsO₄). nH₂O, where n = 6, 7 or 8 depending on the combination, are given in Table 5. (We have prepared the eighth combination, CaKPO₄.nH₂O, 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 MgNH₄PO₄.6H₂O, struvite (Whitaker & Jeffrey, 1970a, b).

The two calcium-ammonium salts,

CaNH₄PO₄.7H₂O and CaNH₄AsO₄.7H₂O, 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 pseudocentering on the C face. This corresponds to the actual centering in CaKAsO₄.8H₂O and the pseudocentering on the C face apparent in the structure of MgNH₄PO₄.6H₂O (Fig. 2). The presence of the

eighth molecule of water in CaKAsO₄ $8H_2O$ 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 AsO₄ oxygen atoms to be the acceptor in four hydrogen bonds. It should also be noted that the n glide operation in MgNH₄PO₄.6H₂O simulates the C centering operation in CaKAsO₄.8H₂O.

Some crystallographic properties for

 $MgKAsO_4.5H_2O$ (TVA, unpublished data),

 $Mg_2KH(PO_4)_2.15H_2O$ and $MgHPO_4.7H_2O$ (Lehr *et al.*, 1967) are given in Table 6. Systematic weaknesses in the X-ray reflections of $MgKAsO_4.5H_2O$ suggest that it has a pseudo-cell a third the size of its real cell. This pseudo-cell closely resembles the pseudohexagonal cell of $MgNH_4PO_4.6H_2O$, described by Whitaker & Jeffery (1970*a*), which corresponds to the primitive cell of CaKAsO_4.8H_2O. The pseudo-cells of MgKAsO_4.5H_2O and MgNHPO_4.6H_2O are compared in the following tabulation:

	MgKAsO4.5H2O	MgNH ₄ PO ₄ .6H ₂ O
	pseudo-cell	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 MgKAsO₄.5H₂O 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 AsO₄ oxygen atom in the magnesium coordination.

From a comparison of the formulae,

 $Mg_2KH(PO_4)_2$.15H₂O (Table 6) is related in composition to $MgNH_4PO_4$.6H₂O, struvite, and

MgHPO₄.7H₂O, the mineral phosphoroesslerite (Table 6). The unit-cell dimensions of Mg₂KH(PO₄)₂.15H₂O clearly resemble those of MgNH₄PO₄.6H₂O, the greater length of b (12·29 as compared to 11·10 Å for MgKPO₄.6H₂O) possibly reflecting the presence of more waters of hydration in the same way as for the salts in Table 5. The cell dimensions of MgHPO₄.7H₂O

are simply related to those of MgNH₄PO₄.6H₂O, but the space group of this compound contains additional symmetry elements ($\overline{1}$ and A) so that a structural relationship to the other two salts in Table 6 is not readily apparent. If the formula is written

 $Mg(H_3O)PO_4.6H_2O$, the chemical relationship to $MgNH_4PO_4.6H_2O$ 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, CaKAsO₄.8H₂O and MgNH₄PO₄.6H₂O, differ considerably in detail. Each of the Ca and K ions in CaKAsO₄.8H₂O has a coordination polyhedron of eight water molecules; the Mg ion in MgNH₄PO₄.6H₂O is coordinated to only

Table 5. Some co	mpounds with	the	'struvite-type'	structure
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	CaKAsO ₄	$CaNH_4PO^*$	$CaNH_4AsO_4^+$.7H ₂ O	MgNH4PO4	‡ MgNH4/ .6H2O	AsO ₄ MgKPO	4* MgKAsO4 .6H2O
Unit-cell dimensions, Å	101120				2 .		- -
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
с	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	<i>P</i> 2 ₁	P21	$Pm2_1n$	$Pm2_1n$	$Pm2_1n$	$Pm2_1n$
\vec{Z} , formula weights per unit cel	12	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	1.5184	1.477	1.503
N_y	1.516	1.4975	1.516	1.4973	1.519	1.481	1.509
Nz	1.519	1.514	1.535	1.505	1.528	1.487	1.5094
Optic sign	(-)	(+)	(+)	(+)	(+)	(+)	(-)
Optic angle $2V^{\circ}$: measured	46–47	41.5	34	41	25	-	22 ·5
calculated	43	43	36	45	29	7 9	29
Dispersion	r > v moderate	none	none	r>v weak	none	r > v weak	r>v moderate
Optic axial plane	(100)	\sim (001)	\sim (001)	(010)	(001)	(001)	(001)
Extinction angle $z \wedge a$. ,						
(in obtuse beta)	-	6°	6.2°	-		-	-
Orientation: N_x	Ь	Ь	Ь	а	b	Ь	Ь
N_y	а	$\sim a$	$\sim a$	Ь	а	а	а
Ňz	с	~ c	$\sim c$	с	с	с	с

* Lehr et al., (1967).

† TVA, unpublished work.

‡ Whitaker & Jeffrey (1970a).

	1	5	
	Mg ₂ KH(PO ₄) ₂ .15H ₂ O*	MgHPO4.7H2O†	MgKAsO4.5H2O‡
а	6·55 Å	11·35 Å	10·79 Å
b	12.29	25.36	10.79
с	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	m triclinic	monoclinic	hexagonal
Space group	$P1$ or $P\overline{1}$	A2/a	<i>P</i> 3 <i>c</i> 1 or <i>P</i> 3 <i>c</i> 1

Table 6. Other probable members of the struvite series

* Lehr et al. (1967).

† Hägele & Machatschki (1939).

‡ TVA, unpublished work.

six water molecules, and the NH₄ ion is coordinated to five water oxygen atoms and one PO₄ oxygen atom. The Ca and K ions share a square configuration of water oxygen atoms; the Mg and NH₄ ions share a triangular configuration. Each of the AsO₄ oxygen atoms in CaKAsO₄.8H₂O is the acceptor in four hydrogen bonds; each of the PO₄ oxygen atoms in $MgNH_4PO_4.6H_2O$ is the acceptor in only three hydrogen bonds. The PO₄ group is positioned so that the NH_4 ion hydrogen bonds to O(1) of the PO₄ group (Whitaker & Jeffrey, 1970a, b) and to water oxygen atoms. In CaKAsO₄.8H₂O, the AsO₄ group (in a special position at the intersection of two mirror planes) cannot have the orientation PO₄ has in $MgNH_4PO_4$ $6H_2O_5$ and its orientation is such that the oxygen atoms are not near the K ion.

MgNH₄PO₄. $6H_2O$ 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 MgHPO₄. $3H_2O$, newberyite (Sutor, 1967).

 $CaNH_4PO_4.7H_2O$, the calcium analogue of struvite, is very unstable and decomposes to $Ca_5(PO_4)_3OH$, the major inorganic phase in the body, within minutes at room temperature, even in an aqueous environment. (CaKAsO₄.8H₂O was studied here because it was one of the more stable members of the series.) Because of its instability, CaNH₄PO₄.7H₂O 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 CaKAsO₄.8H₂O and its fairly high rate of growth (of the order of 1 mm.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 CaNH₄PO₄.7H₂O 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 CaKAsO₄.8H₂O 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) $M_5(XO_4)_3Y$, the apatite type, of which there are many examples (over 70 are listed in Wyckoff, 1965); $Ca_8H_2(PO_4)_6.5H_2O$ (Brown, 1962; Brown, Smith, Lehr & Frazier, 1962) and $Ca_4O(PO_4)_2$ (Dickens,





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

(ii) MXO₄-sheet containing compounds:

 $CaSO_4.2H_2O$ (Atoji & Rundle, 1958), $CaHPO_4.2H_2O$ (Beevers, 1958; Jones & Smith, 1962; Curry & Jones, 1970), $Ca(H_2PO_4)_2.H_2O$ (Smith, Lehr & Brown, 1955; MacLennan & Beevers, 1956; Jones & Cruickshank, 1961; Dickens & Bowen, 1971b), $CaHPO_4$ (MacLennan & Beevers, 1955; Jones & Cruickshank, 1961; Dickens, Bowen & Brown, 1972), and probably

 $Ca_2NH_4H_7(PO_4)_4.2H_2O$, $Ca_2KH_7(PO_4)_4.2H_2O$ and $CaClH_2PO_4.H_2O$ (Brown, Smith, Lehr & Frazier, 1958) contain corrugated sheets; Ca_2PO_4Cl (Greenblatt, Banks & Post, 1967; 1969) contains planar sheets;

(iii) (M, N, \Box)₄(XO₄)₂ or glaserite-type after K₃Na(SO₄)₂ (glaserite): Ca₅(PO₄)₂SiO₄ (Dickens & Brown, 1971*a*) and Ca₇Mg₉(Ca, Mg)₂(PO₄)₁₂ (Dickens & Brown, 1971*b*) both have structures related to the glaserite structure, but with systematic cation vacancies, denoted \Box in the general formula above;

 α -Ca₃(PO₄)₂ (Ando, 1958; Dickens & Brown, 1971*b*), CaNaPO₄ and Ca₄Na₂(PO₄)₄ (Ando & Matsuno, 1968), and the high temperature solid solution between α -Ca₂SiO₄ and $\bar{\alpha}$ -Ca₃(PO₄)₂ (Berak & Wojciechowska, 1956; Nurse, Welch & Gutt, 1959; Dickens & Brown, 1971*a*) may be other examples of glaserite-type structures with systematic cation vacancies; CaK₃H(PO₄)₂ (Brown & Fowler, 1967) is probably a monoclinic distortion of the K₃Na(SO₄)₂ structure.

(iv) $M_3(XO_4)_2$. Compounds with large cations such as $Ba_3(PO_4)_2$ and $Sr_3(PO_4)_2$ (Zachariasen, 1948) and $Ba_3(VO_4)_2$ (Susse & Buerger, 1970) have high symmetry and a small asymmetric unit. $Ca_3(AsO_4)_2$ (Gopal & Calvo, 1971) and β - $Ca_3(PO_4)_2$ formed at ~1000°, or ~1350° with Mg²⁺ as impurity (Dickens, Bowen & Brown, 1971) crystallize in distorted versions of the $Ba_3(PO_4)_2$ structure. Synthetic whitlockite, grown hydrothermally, (Ca, Mg)₂₀H₂(PO₄)₁₄, has an even more distorted version of this structural type (Calvo & Ito, 1972).

(v) $M^{2+}N^{+}XO_{4}$. $nH_{2}O_{4}$, or struvite-type after

MgNH₄PO₄.6H₂O (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 investigation was supported in part by Research Grant DE00572 to the American Dental Association from 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; The United States Army Medical Research and Development Command; the Dental Sciences Division of the School of Aerospace Medicine, USAF; the National Institute of Dental Research; and the Veterans Administration.

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The Crystal Structures of Free Radical Salts and Complexes. IV. $(1,1'-Ethylene-2,2'-bipyridylium)^{2+}-(7,7,8,8-Tetracyanoquinodimethane^{-})_2$

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Crystals of $(C_{12}H_{12}N_2)^{2+}(C_{12}H_4N_4^{-})_2$ 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'bipyridylium)²⁺ (TCNQ⁻)₂ is reported.

Experimental

Crystal data $(C_{12}H_{12}N_2) (C_{12}H_4N_4)_2$, M.W. 592·6, Triclinic, $a = 7.416 \pm 0.001$, $b = 13.371 \pm 0.001$, $c = 14.625 \pm 0.001$ Å, $\begin{aligned} &\alpha = 87.800 \pm 0.004^{\circ}, \ \beta = 95.567 \pm 0.004^{\circ}, \\ &\gamma = 95.200 \pm 0.005^{\circ}, \\ &U = 1436.8 \text{ Å}^3; \\ &D_m = 1.36 \text{ g.cm}^{-3}, \ Z = 2, \ D_c = 1.37 \text{ g.cm}^{-3}, \\ &F(000) = 612. \\ &\text{Mo } K\alpha \ (\lambda = 0.7107 \text{ Å}), \ \mu = 0.94 \text{ cm}^{-1}. \\ &\text{Space group } P \overline{1} \ (\text{assumed}). \end{aligned}$

Purple lath-shaped crystals of the complex salt were obtained when 1 mole of 1,1'-ethylene-2,2'-bipyridylium 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