The crystal structure
of Görgeyite $K_2SO_4 \cdot 5\,CaSO_4 \cdot H_2O$

G. W. Smith and R. Walls

The British Petroleum Company Limited, BP Research Centre,
Chertsey Road, Sunbury-on-Thames, Middlesex, England

Abstract. The crystal structure of the mineral görgeyite, K_2SO_4 $\cdot 5\,CaSO_4 \cdot H_2O$, has been determined from visually estimated photographic intensities using the direct methods program MULTAN, and refined by block-diagonal least-squares structure factors to an R value of 0.096. The mineral is monoclinic and contains four formula units in a cell of dimensions $a = 17.51(1), b = 6.822(5), c = 18.21(1)$ Å, $\beta = 113.3°$ and space group $C2/c$.

Two independent calcium atoms, one of which sits on the diad axis, are nine-fold coordinated by oxygen atoms in a closely similar arrangement, with average $Ca-O$ distances of 2.52 Å in the range $2.40-2.68$ Å. A third calcium atom is eight-fold coordinated with a mean $Ca-O$ distance of 2.46 Å in a range of $2.37-2.64$ Å.

The potassium atom is also eight-fold coordinated. The three independent sulphate ions are approximately regular with mean $S-O$ distances of 1.472(8), 1.477(27), and 1.470(7) Å respectively but their behaviour in providing oxygen coordination is different for each. The hydrogen atom of the water molecule has not been positively located though it is likely that a hydrogen bond is present.

Introduction

The mineral görgeyite was first described in 1953 by Mayrhofer and later that year a sulphate mineral of similar composition called mikheevite was discovered by Nefedov and reported upon by Mokievsky (1953). Fleischer (1955) suggested that the two specimens were identical and following publication of further data by Nefedov (1955), Meixner (1955) confirmed the identity. The present authors (1964) reported a third occurrence of the mineral in drill-cuttings from a borehole at Astakós in Western Greece where it occurred sparingly with halite, anhydrite, gypsum, and polyhalite in a

Triassic evaporite sequence (vide British Petroleum (1971)]. Optical data
($\alpha = 1.560$; $\beta = 1.570$; $\gamma = 1.584$; $2\,V_\gamma = 81°$) are close to Mayrhofer's values
on the type material (Mayrhofer, 1953) and to those of Krüll and Vetter
(1933) on synthetic potassium pentacalcium sulphate. We now report the
structure determination of our sample.

Experimental

As described by Smith, Walls and Whyman (1964) the irregular form of the
sample led initially to a triclinic cell whose parameters were obtained from
zero layer Weissenberg photographs about each of the axes using CuKα
radiation ($\lambda = 1.5418$ Å). The shortest triclinic axis a was found to be a two-
fold symmetry axis and upon transformation, the true monoclinic lattice
parameters were determined as listed in Table 1. These data are in close
agreement with those published by Braitsch (1965). Space group extinctions
were $(h + k) =$ odd for all hkl reflections and $l =$ odd for the $h0l$ zone leading
to either $C2/c$ or Cc. As Mayrhofer (1953) determined the crystal class as
$2/m$, the centrosymmetric space group was taken as correct which has been
justified by an analysis of the intensity statistics and the successful structure
determination. The density of the crystal was obtained by a flotation method.

An irregular shaped crystal fragment, of approximate linear dimension of
0.2 mm was used to collect the intensity data. Intensities were measured by
visual comparison with a calibrated scale from equi-inclination Weissenberg
photographs taken about the b axis for the layers $k = 0 - 5$. Additional
photographs were also taken about the [$\bar{1}\bar{1}0$] axis, i.e. the c axis of the triclinic
cell. In all 1684 reflexions were measured and corrected for the Lorentz-
polarisation factors.

No absorption correction was made and an overall scale and temperature
factor was obtained from a Wilson plot. The $N(z)$ test, Howells, Phillips, and

Table 1. Crystal data

$K_2SO_4 \cdot 5\,CaSO_4 \cdot H_2O$; Formula weight $= 873.0$ (0 $= 16$).	
Monoclinic $C2/c$, $Z = 4$	
a	$= 17.51(1)$ Å
b	$= 6.822(5)$ Å
c	$= 18.21(1)$ Å
β	$= 113.3(1)°$
V	$= 1998.0$ Å^3
D_x	$= 2.90\,g \cdot cm^{-3}$
D_m	$= 2.91(1)$,
$\mu\,(CuK\alpha)$	$= 227\,cm^{-1}$

Rogers (1950) gave a distribution very close to the hypercentric case confirming the choice of space group.

Structure Determination

The structure was solved by the automatic direct methods program MULTAN, (Germain, Main, Woolfson (1971)] for which the data were converted to normalised structure factors and 175 reflexions selected with $E \geq 1.5$. The unit cell contains four water molecules which must by symmetry be sited upon the two-fold axis. It is most likely that the remaining atoms would lie in general positions except for four calcium atoms which could lie, either on the two-fold axis or on a centre of symmetry. The correct solution would therefore exhibit these features.

Within the data set, there were six reflexions with a Σ_1 probability of greater than 0.99 which, taken with the two best origin reflexions selected by MULTAN, formed the starting set. Using five other starting reflexions, two of the sixteen alternative solutions had very low figures of merit and very high residuals and could therefore be rejected. The remaining sets had identical values of both criteria, and a scan of the sign combinations revealed that these fourteen solutions fell into two groups of seven sets each. Accordingly E maps were calculated for one solution from each group. One map showed a string of seven regularly spaced strong peaks, at nearly the same y coordinate, with a strong and a weak peak on the diad, while the other map contained a similar string of peaks, none of which were sited on a special position. The former map could therefore be taken to be the correct solution.

The formal identication of the non-oxygen atoms could not be made upon the basis of peak heights, which decreased linearly along the string from ~ 1150 for the atom on the diad to about 500 for the last. However, since the atom on the diad must be calcium, its nearest neighbour must be sulphur followed by another metal atom and so on. The sequence would then be Ca, S, M, S, M, S, M where M could be either calcium or potassium; but, as both these ions are iso-electronic, further distinction could not be made at this stage. There were many much smaller peaks, with heights ~ 100, making the positions of the oxygen atoms uncertain. These lesser peaks were situated around all the major peaks while those around the tentatively identified sulphur atoms did not form regular tetrahedra. After a few trial structure factor/Fourier calculations, acceptable oxygen positions were obtained which also provided evidence, on the basis of cation-oxygen distances, that the last heavy peak in the sequence was indeed potassium.

Refinement

The structure was refined by a block-diagonal least-squares refinement of structure factors. Isotropic refinements of all atoms, except hydrogen, was

Table 2. Observed and calculated structure amplitudes all values are × 10. Unobserved reflexions denoted by * and evaluated for one half of the lowest intensity value observed in the layer concerned

Table 3. Atomic parameters. Estimated standard deviations are given in parenthesis

Atom	x	y	z
Ca(1)	0.0000	0.0881(4)	0.7500
Ca(2)	0.1487(1)	0.0767(3)	0.4831(1)
Ca(3)	0.2824(1)	0.1261(3)	0.2068(1)
K	0.4330(1)	0.1082(4)	0.9104(1)
S(1)	0.0756(1)	0.0999(4)	0.6170(1)
S(2)	0.2157(1)	0.1129(3)	0.3461(1)
S(3)	0.3682(1)	0.0839(4)	0.0885(1)
O(11)	0.1445(4)	−0.0324(10)	0.6224(3)
O(12)	0.0530(4)	0.2130(11)	0.5427(4)
O(13)	0.1015(4)	0.2323(11)	0.6854(4)
O(14)	0.0060(4)	−0.0190(11)	0.6195(4)
O(21)	0.2641(3)	−0.0421(10)	0.3224(3)
O(22)	0.1365(4)	0.0300(11)	0.3415(4)
O(23)	0.2037(3)	0.2784(11)	0.2904(3)
O(24)	0.2619(3)	0.1686(11)	0.4284(3)
O(31)	0.3991(4)	−0.1086(11)	0.0764(4)
O(32)	0.2801(3)	0.0762(10)	0.0749(3)
O(33)	0.4119(3)	0.1391(10)	0.1736(3)
O(34)	0.3814(3)	0.2329(10)	0.0366(3)
O(1)	0.5000	0.2264(20)	0.7500

continued until $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o| = 0.145$. The weighting scheme was of the type $w = 1$ for $F \leq 25.0$ and $w = 25/F$ for $F > 25$. Optimum layer scale factors were calculated at intervals by a method due to Eichhorn (1956) and atomic scattering factors for the neutral atoms were taken from International Tables. Scattering factors for Ca^{2+} and K^+ were next introduced and the refinement continued using anistropic temperature factors for the cations and sulphur atoms and isotropic factors for the oxygen atoms. The weighting was changed in the last few cycles to $w^{-1} = 50 + F + 0.005\,F^2$ until the refinement converged at $R = 0.096$ for 1657 reflexions. Electron density and difference maps were calculated at intervals throughout the refinement process but at no stage was it possible to locate with certainty the position of the hydrogen atom of the water molecule. The calculated and observed structure factors are listed in Table 2 and the atomic parameters in Tables 3 and 4. The oxygen numbering is such that the first digit refers to the sulphur atom to which they are attached and the second digit is the sequence number. O(1) is the oxygen of the water molecule.

In the description that follows there are two factors to be borne in mind which are likely to affect the overall accuracy of the structure. As is well known the use of the block-diagonal approximation in least-squares refinements leads to standard deviations which are lower by a factor of between two and three than would have been obtained from full-matrix methods.

Table 4. Anisotropic thermal parameters β_{ij} and isotropic temperature factors B with standard deviation in parentheses. The β_{ij} values are multiplied $\times 10^5$ and the expression used is exp $-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{23}kl + \beta_{13}hl + \beta_{12}hk)$

Atom	B	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
Ca(1)		14(7)	320(77)	48(7)	0	− 6(11)	0
Ca(2)		22(5)	168(53)	47(5)	65(23)	4(8)	69(22)
Ca(3)		15(5)	167(53)	40(5)	19(23)	−13(8)	48(21)
K		75(6)	514(68)	186(7)	−46(33)	− 3(11)	68(28)
S(1)		11(6)	599(73)	70(6)	−60(30)	− 5(10)	−58(27)
S(2)		27(6)	114(64)	28(5)	18(27)	5(9)	−28(26)
S(3)		32(6)	317(67)	32(6)	27(28)	−38(10)	−10(27)
O(11)	0.89(10)						
O(12)	1.27(11)						
O(13)	0.99(10)						
O(14)	1.00(10)						
O(21)	0.83(10)						
O(22)	0.96(10)						
O(23)	0.85(9)						
O(24)	0.93(10)						
O(31)	1.25(11)						
O(32)	0.79(9)						
O(33)	0.82(10)						
O(34)	0.59(10)						
O(11)	2.80(22)						

Therefore allowance for this should be made in comparing bond lengths calculated from this structure with those of other sulphate structures.

Secondly no absorption correction was applied because of the extremely irregular shape of the crystal fragment. However the average linear dimension was not too far removed from the optimum crystal size given by the expression $2/\mu$. Hence the absence of a suitable correction while not large enough to cause serious error in the positional parameters, is likely to show its largest effect upon the temperature parameters.

Description of the structure

A stereoscopic drawing by ORTEP, (Johnson (1965)] of the unit cell contents is shown in Fig. 1. Unlike the structure of anhydrite, (Morikawa et al. (1975)] and gypsum, [Cole and Lancucki (1974)], all three sulphate ions are independent. The S—O bond lengths, Table 5 show a variation within each sulphate group, although all are within 2σ of their respective mean S—O distances of 1.472(8), 1.477(27) and 1.470(7) Å, which are themselves close to the observed values in anhydrite and potassium sulphate [McGinnety (1972)]. There are no symmetry requirements for the sulphate anions but as Table 5 shows the geometrical features of the ions are close to a regular terahedron.

Table 5. Interatomic distances [Å] and tetrahedral angles [°] in the sulphate ions

Atoms	Distance	Angle	Atoms	Distance	Angle
S(1)—O(11)	1.478(7)		S(3)—O(31)	1.470(8)	
—O(12)	1.469(7)		—O(32)	1.463(7)	
—O(13)	1.459(7)		—O(33)	1.481(6)	
—O(14)	1.480(7)		—O(34)	1.467(7)	
Mean	1.472(8)		Mean	1.470(7)	
O(11)—O(12)	2.374(10)	107.3(0.4)	O(31)—O(32)	2.427(10)	111.7(0.4)
—O(13)	2.413(10)	110.5(0.4)	—O(33)	2.393(9)	108.4(0.4)
—O(14)	2.406(9)	108.9(0.4)	—O(34)	2.423(10)	111.2(0.4)
O(12)—O(13)	2.398(8)	110.0(0.4)	O(32)—O(33)	2.337(9)	105.1(0.4)
—O(14)	2.460(10)	113.0(0.4)	—O(34)	2.399(9)	109.9(0.4)
O(13)—O(14)	2.365(10)	107.2(0.4)	O(33)—O(34)	2.422(8)	110.5(0.4)
Mean	2.403(31)	109.5(2.0)	Mean	2.400(31)	109.5(2.2)
S(2)—O(21)	1.520(7)				
—O(22)	1.468(7)				
—O(23)	1.477(7)				
—O(24)	1.444(6)				
Mean	1.477(27)				
O(21)—O(22)	2.442(9)	109.6(0.4)			
—O(23)	2.398(10)	106.3(0.4)			
—O(24)	2.419(9)	109.4(0.4)			
O(22)—O(23)	2.447(10)	112.4(0.4)			
—O(24)	2.339(9)	106.9(0.4)			
O(23)—O(24)	2.428(8)	112.4(0.4)			
Mean	2.412(36)	109.5(2.4)			

The mean tetrahedral angles are 109.5(2.0)°, 109.5(2.4)°, and 109.5(2.2)° for each ion respectively with all angles inside the $2\,\sigma$ limit. The mean $O-O$ distances around the edges are respectively 2.40(0.3) Å, 2.41(0.4) Å, and 2.40(0.3) Å, with no individual distance outside the $2\,\sigma$ limit, and all are very close to the 2.41 Å to be found in gypsum.

However, the behaviour of each sulphate ion in providing the oxygen coordination for the cations is quite different and could provide the explanation of the greater distortion of the ion centred on S(2). For instance, the oxygens around S(3) are each used only twice, Table 6, and provide 8
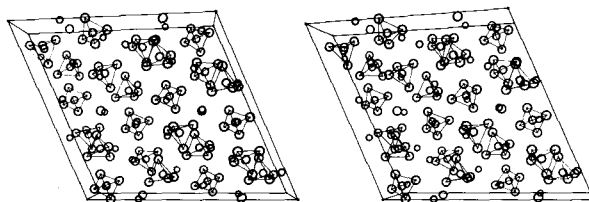
Fig. 1. Stereoscopic view of unit cell contents looking down b axis with c axis horizontal

contacts to separate cations, while the S(1) oxygen atoms are each used three times and provide two pairs of symmetrical contacts with Ca(1), three with Ca(2), two with Ca(3) and five contacts with the potassium ion where O(12) is used twice and has two distinct distances. The central sulphate ion on S(2) is intermediate between the other two. Its oxygen atoms form nine contacts of which four are connected to Ca(3), three with Ca(2) but only one with Ca(1). The sole contact with the K ion comes from O(21) which is the only oxygen atom of this group to have three cation contacts and it is also the oxygen atom which has the extra long S — O distance. The other three oxygen atoms in the group have two contacts each. O(23) has two distinct distances with Ca(3) and O(24) two separate distances with Ca(2), while O(22) is coordinated to both Ca(1) and Ca(2).

The calcium atoms have two different types of coordination. Ca(1) and Ca(2) are nine-fold coordinated while Ca(3) is only eight-fold as is the K ion. This compares with eight-fold coordinated calcium in gypsum and anhydrite. The nine-fold polyhedron around Ca(1) contains the diad axis which passes through the water oxygen O(1) and the centre of the O(33) — O(33) distance across the diad. The average Ca — O distance is 2.52 Å, with a range of 2.45 — 2.68 Å, while the O — O nearest neighbour distances, around the polyhedron vary considerably from 2.37 Å for O(13) — O(14) derived from the sulphate group around S(1) to 3.42 Å for O(33) — O(14). There is a large almost planar face bounded by O(1), O(14), O(13) and O(22). The distance O(14) — O(22) of 3.78 Å corresponds to the shorter diagonal of this face. The other nine-fold coordination around Ca(2) closely parallels that around Ca(1). The average Ca — O distance is 2.53 Å with a range of 2.40 — 2.67 Å and even though there is no symmetry present there is a tendency towards a two-fold axis. The final result is less skew and the polyhedron is more equi-dimensional. Table 7 compares the O — O distances of the two polyhedra in which O(34) corresponds to O(1) and O(24) — O(31) equates to O(33) — O(33). There are two short distances of 2.37 Å and 2.34 Å for O(11) — O(12) and O(24) — O(22) arising from the sulphate tetrahedra while the longest distances are now 3.17 Å, O(31) — O(24); 3.18 Å, O(24) — O(12) and 3.18 Å O(34) — O(11). The comparable large nearly planar faces are O(22), O(24), O(32), O(34) and O(11), O(12), O(14), O(34).

Table 6. Cation-oxygen distances [Å]. Standard deviations are in parentheses. Code for symmetry operation is given below

	Ca(1)	Ca(2)	Ca(3)	K
O(11)		2.672(6)(i)	2.380(7)(iii)	2.754(7)(viii)
O(12)		2.506(7)(i)		2.810(8)(viii)
				2.774(7)(vii)
O(13)	2.676(7) (i)		2.401(7)(vi)	3.024(7)(viii)
O(14)	2.528(6) (i)	2.643(7)(ii)		2.889(8)(viii)
O(21)			2.526(6)(i)	2.793(7)(iii)
			2.393(7)(viii)	
O(22)	2.448(7)(ii)	2.523(6)(i)	3.371(7)(viii)	
O(23)			2.636(7)(i)	
			2.383(7)(viii)	
O(24)		2.622(7)(i)		
		2.464(7)(vi)		
O(31)		2.402(8)(viii)		2.847(8)(ii)
O(32)		2.477(6)(iii)	2.410(6)(i)	
O(33)	2.466(7) (vi)		2.569(7)(i)	
O(34)		2.399(7)(viii)		2.913(6)(i)
O(1)	2.467(14)(v)			
Mean	2.517	2.525	2.462	2.851

Symmetry Code:
(i) x, y, z.
(ii) $\bar{x}, \bar{y}, 1-z$
(iii) $x, \bar{y}, \frac{1}{2}+z$
(iv) $\bar{x}, y, \frac{1}{2}-z$
(v) $\frac{1}{2}+x, \frac{1}{2}+y, z$
(vi) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$
(vii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
(viii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

The third calcium atom is eight-fold coordinated in a similar manner to gypsum and anhydrite. The $Ca - O$ distances lie in the range 2.37 Å $-$ 2.64 Å with a mean of 2.46 Å which is very close to the 2.46 Å and 2.47 Å found, respectively, in the other structures. Around the polyhedron, $O - O$ distances vary from 2.34 Å for $O(32) - O(33)$ up to 3.91 Å for $O(13) - O(23)$, but sitting above the large almost flat face bounded by $O(13)$, $O(21)$, $O(32)$, and $O(33)$ there lies $O(22)$ which because it is at 3.37 Å from Ca(3) cannot be said to form part of the first coordination shell around Ca(3). It does, however, form contacts with these four oxygen atoms at respective distances of 3.21 Å, 2.44 Å, 3.50 Å and 2.78 Å and can therefore be considered as making an attempt to increase the coordination number of this calcium ion from eight to nine.

The potassium ion is also eight-fold coordinated with cation-oxygen distances in the range 2.75 Å $-$ 3.02 Å. The mean value of 2.85 Å is greater than the 2.74 Å to be found in potassium sulphate. This coordination polyhedron also differs from those around the calcium ions because it is linked by a shared edge $O(12) - O(12)$, to its symmetry related image across the centre of symmetry at $\frac{1}{2}, 0, 0$. The $O - O$ distances have a much larger

Table 7. Nearest oxygen-oxygen distances [Å] in the cation coordination polyhedra

Nine-fold coordination				Eight-fold coordination			
Ca(1)		Ca(2)		Ca(3)		K	
Atoms	Distance	Atoms	Distance	Atoms	Distance	Atoms	Distance
O(33) vi – O(33) vii	3.235	O(24) vi – O(31)	2.842	O(11) – O(21) i	3.446	O(11) – O(12) vii	3.781
O(33) vi – O(13) i	2.810	O(24) vi – O(24) i	3.008	O(11) – O(21) viii	3.276	O(11) – O(14)	2.406
		O(31) – O(12)	2.884	O(11) – O(23) i	3.277	O(11) – O(21)	3.276
O(33) vii – O(13) i	3.358	O(31) – O(24) i	3.174	O(11) – O(23) viii	3.041	O(11) – O(34)	3.180
O(33) vii – O(22)	2.779	O(24) vi – O(12)	3.177	O(11) – O(32)	2.845	O(12) vii – O(12) viii	4.350
		O(24) vi – O(32)	2.870	O(13) – O(21) i	3.208	O(12) vii – O(14)	3.021
O(33) vii – O(14)	3.418	O(31) – O(14)	3.067	O(13) – O(21) viii	3.224	O(12) vii – O(31)	2.883
O(1) – O(22)	2.843	O(31) – O(22)	3.074	O(13) – O(23) i	3.262	O(12) vii – O(34)	2.987
		O(24) vi – O(11)	3.299	O(13) – O(23) viii	3.910	O(12) viii – O(13)	2.398
O(1) – O(14)	2.974	O(34) – O(14)	2.873	O(13) – O(33)	2.809	O(12) viii – O(21)	3.888
O(14) – O(22)	2.854	O(34) – O(32)	3.046	O(21) i – O(23) i	2.398	O(12) viii – O(31)	4.029
		O(34) – O(22)	3.113	O(21) i – O(23) viii	2.636	O(12) viii – O(34)	4.159
O(14) – O(22)	3.777	O(34) – O(11)	3.182	O(21) viii – O(23) i	2.636	O(13) – O(14)	5.361
		O(11) – O(32)	2.846	O(21) viii – O(32)	3.467	O(13) – O(21)	3.208
O(13) – O(22)	3.204	O(14) – O(22)	2.854	O(21) viii – O(33)	3.796	O(13) – O(31)	4.187
		O(22) – O(32)	4.058	O(23) viii – O(32)	3.110	O(14) – O(21)	4.787
O(13) – O(14)	2.365	O(11) – O(14)	4.160	O(32) – O(33)	2.338	O(14) – O(31)	3.068
		O(12) – O(14)	3.021	O(22) – O(13)	3.206	O(21) – O(34)	3.846
		O(24) i – O(32)	3.054	O(22) – O(21)	2.442		
		O(24) i – O(22)	2.340	O(22) – O(32)	3.504		
		O(12) – O(11)	2.374	O(22) – O(33)	2.779		

Symmetry Code:

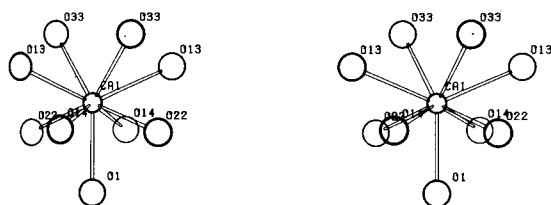|			
i	x, y, z.	v	$\frac{1}{2} + x, \frac{1}{2} + y, z$
ii	$\bar{x}, \bar{y}, 1 - z$	vi	$\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
iii	$x, \bar{y}, \frac{1}{2} + z$	vii	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
iv	$\bar{x}, y, \frac{1}{2} - z$	viii	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

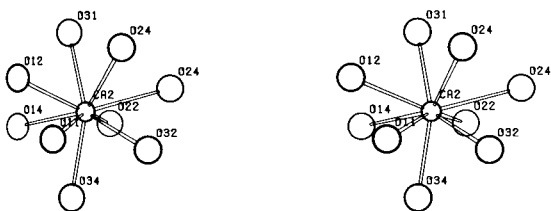**Fig. 2.** Stereoscopic view of oxygen coordination around Ca(1)

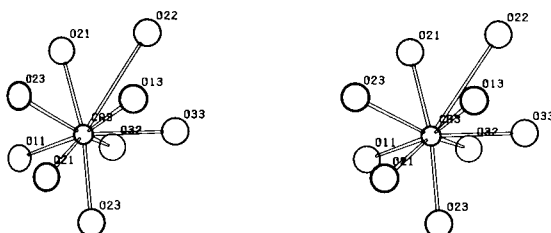**Fig. 3.** Stereoscopic view of oxygen coordination around Ca(2)

Fig. 4. Stereoscopic view of oxygen coordination around Ca(3) with the extra atom O(22)
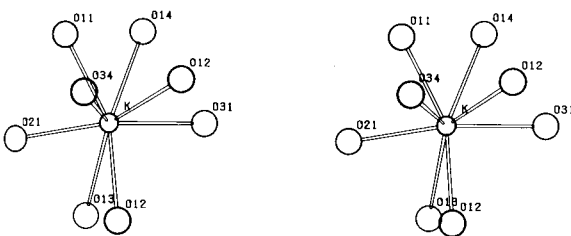

Fig. 5. Stereoscopic view of oxygen coordination around K

range of 2.40 Å — 4.35 Å. The coordination around each cation is shown in stereoscopic drawings in Figures 2 — 5.

In the absence of an unequivocal position for the hydrogen atom it is not possible to discuss with certainty the role of the water molecule and the formation of hydrogen bonding if any. If a hydrogen bond is present, then the

likely bonded oxygen would be O(22) which lies at 2.85 Å from O(1) compared with O(14) at 2.97 Å, O(33) at 2.97 Å O(31) at 3.06 Å and O(23) at 3.35 Å. Attempts were made to include the hydrogen atom in the refinement process in a likely position between O(1) and O(22) but the errors in the photographic data yielded an unacceptable temperature factor. Unlike gypsum however, the two hydrogen bonds, if present, would be equal by symmetry. An infra-red spectrum taken of a synthetic preparation of this compound indicates that there is some hydrogen bonding present but that it is not very strong.

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