Crystal Structure of Anhydrous Potassium Carbonate

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Crystals of the title compound are monoclinic, space group $P2_1/c$ with unit cell dimensions: $a = 5{\cdot}64$, $b = 9{\cdot}80$, $c = 6{\cdot}88$ Å, $\beta = 98{\cdot}8°$. The structure, which was determined from photographic *X*-ray data by Patterson and Fourier methods, consists of a slightly distorted hexagonal close packed array of carbonate ions in which potassium ions occupy both octahedral and trigonal bipyramidal sites. The carbonate ions have non-crystallographic trigonal planar geometry to within the accuracy of this determination. The structure was refined by least-squares methods to *R* 0·129 for 316 observed reflections.

ATTEMPTS to prepare crystalline compounds in the K_2O–ZrO_2 system, in particular the hexagonal α-form of $K_2Zr_2O_5$,[1] produced clear, hygroscopic pseudo-hexagonal plate-like crystals. The preparation involved dissolving zirconia in molten decomposing potassium nitrate in open Pythagoras furnace-ware over a coal-gas burner. The crystals were apparent, growing from the bulk material after several hours at *ca.* 830 °C and were 1—2 mm in width after several days. They were identified as anhydrous potassium carbonate from their i.r. spectrum,[2] and from the *X*-ray powder data (see preparation). Since the structure of this material has not been reported previously, a three-dimensional single-crystal structure determination has been carried out and is described here.

EXPERIMENTAL

Preparation.—Crystals of anhydrous potassium carbonate were grown by the method outlined in the introduction; however, two essential features of the preparation were the presence of ZrO_2 (or SnO_2) and the coal gas available at Monash University at the time. Reactions attempted without the addition of zirconia resulted in the decomposition of the potassium nitrate and the complete loss by evaporation of the potassium oxide formed. Until at least a week after the conversion of the gas supply to natural gas (from Bass Strait), the preparation was reproducible from zirconia (Hopkins and Williams) and potassium nitrate (AnalarR, B.D.H.). However, attempts 6 months later and subsequently have failed to produce crystals. Similar crystals have been made by heating anhydrous potassium carbonate (Univar, A.R. grade) at 800—830 °C in open Pythagoras furnace-ware by use of a Meker burner with natural gas.

Both single-crystal and powder data agree very well with the data in the '*X*-Ray Powder Data File'[3] with the exception of the $20\bar{1}$ line, which should be systematically absent for space group $P2_1/c$, which is listed as present in the file.

Crystal Data.—K_2CO_3, $M = 138{\cdot}21$, Monoclinic, $a = 5{\cdot}64 \pm 0{\cdot}03$, $b = 9{\cdot}80 \pm 0{\cdot}04$, $c = 6{\cdot}88 \pm 0{\cdot}03$ Å, $\beta = 98{\cdot}8 \pm 0{\cdot}5°$, $U = 375{\cdot}78$ Å^3, $D_c = 2{\cdot}44$, $Z = 4$, D_m[4] $= 2{\cdot}428$. Space group $P2_1/c$ (No. 14), from systematic absences: $h0l$ for l odd, $0k0$ for k odd. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 85·5 cm^{-1}.

An untwinned fragment (0·09 × 0·09 × 0·01 mm) suitable for data collection was obtained by breaking up one of the large multiply twinned pseudo-hexagonal plate-like crystals. This fragment, oriented about the *b* axis (in the plane of the plate) was sealed in a Pyrex capillary, filled with dry paraffin oil, and the cell dimensions obtained from oscillation and Weissenberg photographs. The direction perpendicular to the plate proved to be the pseudo-hexagonal *c* axis.

Intensity data were collected by the multiple-film method for the levels $h0$—$8l$. Visual estimation by use of a calibrated strip proved difficult owing to the very small diffraction spots which resulted from the use of a crystal well below optimum size. The data were measured by two independent observers and the agreement between

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[1] B. M. Gatehouse and D. J. Lloyd, *J. Solid-State Chem.*, 1970, **1**, 478.

[2] C. J. H. Schutte and K. Buijs, *Spectrochim. Acta*, 1961, **17**, 921.

[3] '*X*-Ray Power Data File,' American Society for Testing Materials Inorganic Card 16 820, 1966.

[4] 'Handbook of Chemistry and Physics,' 48th edn., The Chemical Rubber Co., Cleveland, Ohio, 1962.

the two sets of intensities using a conventional R factor was 0·056. The mean values were used in the structure determination.

Structure Determination and Refinement.—Corrections were applied for Lorentz and polarization effects and the three-dimensional Patterson synthesis was solved for the position of one potassium atom by use of the Harker heavy atom method. The complete model appeared in subsequent Fourier and difference-Fourier syntheses based on the single potassium atom position. Scattering curves used were those for K^+, C^0, and O^0 from ref. 5. The application of an absorption correction[6] followed by full-matrix least-squares refinement reduced the agreement for a model with isotropic thermal parameters by *ca.* 2·5% to R 0·129 for the 316 observed reflections and R 0·191 for all 624 reflections. The latter agreement is relatively poor owing to the high proportion of unobserved reflections: the weighted agreement factor R' of 0·160 $\left[R' = \left(\sum_{hkl}\left||F_o| - |F_c|\right|^2\right)^{\frac{1}{2}} \Big/ \left(\sum_{hkl}|F_o|^2\right)^{\frac{1}{2}}\right]$ is perhaps more realistic. The validity of an absorption correction applied for a crystal of such extreme shape and size, neither of which was accurately known, is somewhat doubtful. No corrections were made for the crystal environment.

TABLE 1

Atomic positional and thermal parameters with estimated standard deviations in parentheses

Atom	x	y	z	B/Å^2
K(1)	0·2418(7)	0·0831(6)	0·2144(6)	2·96(10)
K(2)	0·7391(6)	0·2597(5)	0·9754(5)	2·49(09)
C	0·250(3)	0·420(3)	0·243(3)	2·58(34)
O(1)	0·735(2)	0·044(2)	0·199(2)	3·45(27)
O(2)	0·063(2)	0·348(2)	0·276(2)	3·04(25)
O(3)	0·421(2)	0·362(2)	0·173(2)	3·72(29)

The final positional parameters (Table 1) were obtained following least-squares refinement using all reflections, the resulting structure having planar symmetric carbonate ions of essentially D_{3h} symmetry. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 205421 (2 pp., 1 microfiche).* Relevant interatomic distances and angles are given in Table 2. A final three-dimensional difference Fourier synthesis showed no significant maxima or minima.

DISCUSSION

In terms of ionic packing, anhydrous potassium carbonate has a crystal structure which can be described as a slightly distorted hexagonal close-packed (h.c.p.) array of carbonate ions in which the potassium ions occupy both octahedral [K(2)] and trigonal bipyramidal [K(1)] sites with respect to the carbonate ions (see Figure 1). The structures of α- (hexagonal, high-temperature form) and γ-Na_2CO_3 (room-temperature form) have been described[7] and, although no interatomic distances were given for these compounds, the overall co-ordination and structure type are very similar to

TABLE 2

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Up to 3·5 Å

K(1) ··· O(1^{I})	2·83(2)	K(2) ··· O(3^{VIII})	2·61(2)
K(1) ··· O(2^{I})	2·84	K(2) ··· O(1^{VIII})	2·62
K(1) ··· O(1^{II})	2·87	K(2) ··· O(2^{IX})	2·67
K(1) ··· O(2^{III})	2·88	K(2) ··· O(2^{X})	2·69
K(1) ··· O(3^{IV})	2·91	K(2) ··· O(1^{VII})	2·70
K(1) ··· O(3^{I})	2·94	K(2) ··· O(3^{VII})	2·80
K(1) ··· O(2^{V})	3·11		
K(1) ··· O(1^{VI})	3·13		
K(1) ··· O(3^{VII})	3·21		

(*b*) Up to 4 Å

K(1) ··· C^{V}	3·25(2)	K(2) ··· C^{VII}	3·45(2)
K(1) ··· C^{III}	3·25	K(2) ··· C^{XI}	3·49
K(1) ··· C^{IV}	3·26	K(2) ··· C^{X}	3·54
K(1) ··· C^{I}	3·31	K(2) ··· C^{XII}	3·85
K(1) ··· C^{VII}	3·63	K(2) ··· C^{VIII}	3·88
K(1) ··· K(2^{V})	3·45(2)	K(2) ··· C^{IX}	3·92
K(1) ··· K(2^{XIII})	3·51	K(2) ··· K(2^{VII})	3·45(2)
K(1) ··· K(2^{XIV})	3·61	K(2) ··· K(2^{V})	3·45
K(1) ··· K(2^{XII})	3·81	K(2) ··· K(1^{VII})	3·45
K(1) ··· K(2^{XV})	3·87	K(2) ··· K(1^{X})	3·51
K(1) ··· K(2^{XVI})	3·90	K(2) ··· K(1^{XIV})	3·61
		K(2) ··· K(1^{XVII})	3·81
		K(2) ··· K(1^{VIII})	3·87
		K(2) ··· K(1^{IX})	3·90

		Angles	
C–O(1^{XVIII})	1·28(2)	O(1)–C–O(2)	118·0(2·3)
C–O(2^{I})	1·32(2)	O(1)–C–O(3)	122·0
C–O(3^{I})	1·28(2)	O(2)–C–O(3)	120·1
O(1) ··· K(2^{XIX})	2·62(2)	O(2) ··· K(2^{XVI})	2·67(2)
O(1) ··· K(2^{V})	2·70	C(2) ··· K(2^{XIII})	2·69
O(1) ··· K(1^{I})	2·83	O(2) ··· K(1^{I})	2·84
O(1) ··· K(1^{XX})	2·87	O(2) ··· K(1^{XXI})	2·88
O(1) ··· K(1^{VI})	3·13	O(2) ··· K(1^{VII})	3·11
O(3)–K(2^{XV})	2·61(2)	O(2) ··· K(2^{V})	3·99
O(3)–K(2^{V})	2·80	O(1) ··· O(2^{IV})	2·23
O(3)–K(1^{XVIII})	2·91	O(1) ··· O(3^{IV})	2·23
O(3)–K(1^{I})	2·94	O(2) ··· O(3^{I})	2·24
O(3)–K(1^{V})	3·21		
O(3)–K(2^{XI})	3·91		

Roman numerals as superscripts indicate the following equivalent positions:

I	x, y, z	XII	$1 - x, -\frac{1}{2} + y, \frac{3}{2} - z$
II	$-1 + x, y, z$	XIII	$-1 + x, y, -1 + z$
III	$-x, -\frac{1}{2} + y, \frac{1}{2} - z$	XIV	$1 - x, -y, 1 - z$
IV	$1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$	XV	$x, y, -1 + z$
V	$x, \frac{1}{2} - y, -\frac{1}{2} + z$	XVI	$-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$
VI	$1 - x, -y, -z$	XVII	$1 - x, \frac{1}{2} + y, \frac{3}{2} - z$
VII	$x, \frac{1}{2} - y, \frac{1}{2} + z$	XVIII	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
VIII	$x, y, 1 + z$	XIX	$x, y, -1 + z$
IX	$1 + x, \frac{1}{2} - y, \frac{1}{2} + z$	XX	$1 + x, y, z$
X	$1 + x, y, 1 + z$	XXI	$-x, \frac{1}{2} + y, \frac{1}{2} - z$
XI	$1 - x, 1 - y, 1 - z$		

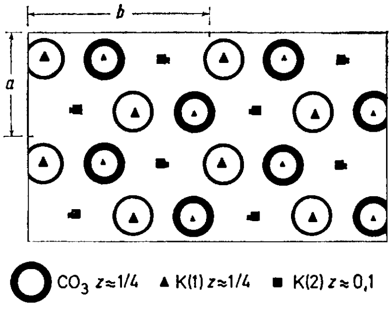

FIGURE 1 A view down the c axis of four unit cells. Carbonate ions are represented by the carbon atom positions

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[5] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[6] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

[7] G. C. Dubbeldam and P. M. de Wolff, *Acta Cryst.*, 1969, **B25**, 2665.

that of potassium carbonate reported here. The sodium analogues seem to be less distorted from an ideal close-packed arrangement than is the potassium compound.

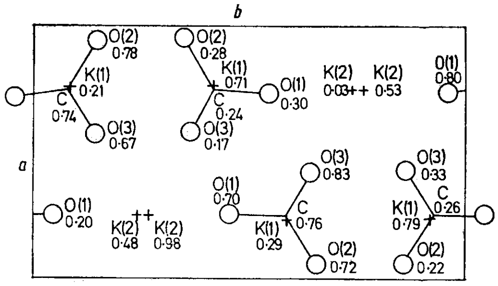

FIGURE 2 A view down the c axis of one unit cell

An alternative description of the structure based on a distorted h.c.p. arrangement of potassium ions [K(1)] and oxygen atoms, *i.e.* in terms of atomic packing, leads to a structural relationship between this compound and $BaNiO_3$. The K(1) atoms are situated in an anion lattice site as, for example, are calcium atoms in perovskite ($CaTiO_3$), where they occupy a site at the centre of a distorted hexagon of oxygen atoms with a triangle of oxygen atoms above and below (see Figure 2). The slight incompatibility of such a site for potassium may be considered to be the cause of distortions present in the structure which are manifested in the ionic model as a tilting of the carbonate ions. The arrangement within each layer is such that three oxygen atoms are almost isolated by surrounding K(1) atoms. The carbon atoms occupy the triangles of oxygen atoms created. The potassium atoms K(2) occupy regular octahedral sites with respect to oxygen atoms and have all six contacts to oxygen atoms of different carbonate groups (Table 2), resulting in unusual, infinite isolated strings of face-shared KO_6 octahedra which are clearly emphasized when this description is used. One quarter of the available octahedral sites are occupied: the remaining positions have unacceptable environments for potassium ions.

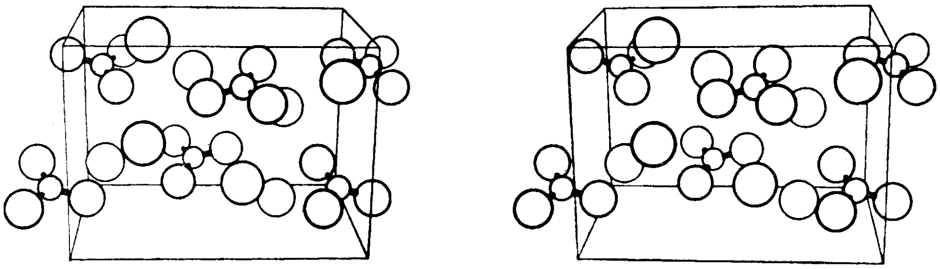

FIGURE 3 A stereoscopic view of the structure; the unit cell is outlined

The $BaNiO_3$ structure [8] can be described as an h.c.p. arrangement of oxygen and barium atoms, with nickel present in one quarter of the octahedral sites forming infinite strings of face-shared NiO_6 octahedra. The difference between the two structures (K_2CO_3 and $BaNiO_3$), is the carbon atom which occupies the trigonal bipyramidal site between the K(1) (or Ba) atoms in the z direction.

This remarkable relationship indicates that the use of atomic (or sphere) packing schemes to describe structures involving polyatomic ions is not only informative but may provide a fundamental lead in the study of transformation mechanisms and structures of crystalline solids.

Within the accuracy of this determination the carbonate ions are symmetric and planar, as may be seen [9] in Figure 3. Figure 4 illustrates the environment of each oxygen atom in the crystallographically unique CO_3 group out to 3·5 Å.

The conversion of potassium nitrate to potassium carbonate in the presence of ZrO_2 or SnO_2 appears to be possible with the aid of some constituent of oxidized coal gas. The observed reactions were not quantitative and no mechanism for the transformation will be suggested here.

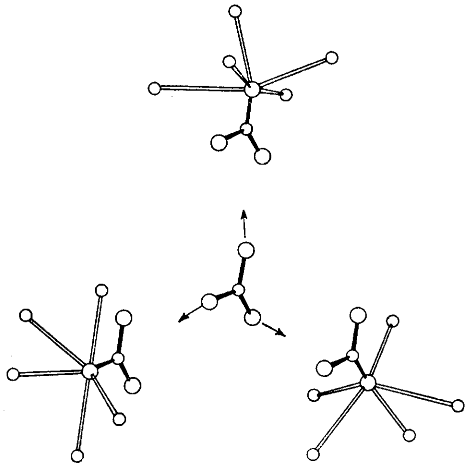

FIGURE 4

We thank the Australian Research Grants Committee for financial support, Monash University for the award of a graduate scholarship (to D. J. L.), and Miss P. R. Buckley for measuring one set of data.

[1/2480 *Received, 29th December*, 1971]

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[8] R. W. G. Wyckoff, 'Crystal Structures,' vol. 2, 2nd edn., Interscience, New York, 1958.

[9] ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, C. K. Johnson, 1965, Oak Ridge National Laboratory, Report ORNL 3794.