521. *A Reinvestigation of the Crystal Structure of Potassium Silver Carbonate.*

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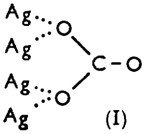
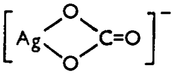
Potassium silver carbonate, $KAgCO_3$, is orthorhombic, with $a = 20{\cdot}50 \pm 0{\cdot}20$, $b = 5{\cdot}82 \pm 0{\cdot}06$, $c = 6{\cdot}00 \pm 0{\cdot}06$ Å, space group *Ibca*, and eight molecules per unit cell. The positions of the potassium and silver atoms were taken as those determined by previous workers; the remaining atoms were located from a three-dimensional electron-density map. The structure consists of chains of silver atoms joined together by carbonate groups in a " *syn-syn* " bridging arrangement. The chains are held together by discrete potassium ions. Each silver atom is covalently bonded to two oxygen atoms (Ag–O distance = 2·09 Å) such that the co-ordination is almost linear (O–Ag–O angle = 170°). There are three close silver–silver distances 3·00, 3·21, and 3·34 Å.

THE crystal structure of potassium silver carbonate was first investigated by Donohue and Helmholz.[1] The co-ordinating oxygen atom of the carbonate group was placed so that it was equidistant from, and co-ordinated to, two silver atoms, making the oxygen atom tercovalent (I). There are some dubious features about the structure as reported. First, the silver–oxygen distance (2·42 Å) is much longer than expected[2] for a covalent bond (*e.g.*, 2·05 Å in Ag_2O[3]); it approaches the sum of the ionic radii of the two atoms (2·70 Å). Also, the co-ordinates of one of the oxygen atoms were assumed on " chemical grounds " and the possibility of linear two-fold co-ordination of the silver atom was ruled out on the basis that a structure of this type would lead to improbable interatomic distances. These results have been interpreted (wrongly) by some as indicating a four-membered ring structure (II);[4] this would be the first verified example of angular two-fold co-ordination of the silver(I) atom. Because of the anomalies in the original investigation we repeated the structure analysis.



(I)



(II)

EXPERIMENTAL

Potassium silver carbonate was prepared by de Schulten's method.[5] Crystals for the *X*-ray study were obtained by Donohue and Helmholz's procedure.[1]

Oscillation and Weissenberg photographs taken about the needle axis showed that the crystal belonged to the orthorhombic system. The observed systematic absences (*hkl* with $h + k + l = 2n + 1$, $0kl$ with $k = 2n + 1$ and $l = 2n + 1$, $h0l$ with $h = 2n + 1$ and $l = 2n + 1$, $hk0$ with $h = 2n + 1$ and $k = 2n + 1$) were compatible with the space group *Ibca* which was established by Donohue and Helmholz from Laue photographs. The cell dimensions, measured from *c*-axis oscillation and zero-layer Weissenberg photographs, compare with those found by previous workers:

	a	*b*	*c*
Present work	20·50	5·82	6·00 Å
Donohue and Helmholz [1]	20·23	5·75	5·95 Å

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[1] Donohue and Helmholz, *J. Amer. Chem. Soc.*, 1944, **66**, 295.

[2] Pauling, " The Nature of the Chemical Bond and the Structure of Molecules and Crystals," Cornell Univ. Press, 3rd edn., 1960, p. 276.

[3] Wyckoff and Posnjak, *J. Amer. Chem. Soc.*, 1922, **44**, 30.

[4] Sidwick, " The Chemical Elements and Their Compounds," Oxford Univ. Press, 1950, p. 145.

[5] de Schulten, *Compt. rend.*, 1887, **105**, 811.

The density quoted by de Schulten[5] is smaller than the calculated value because of contamination with potassium carbonate. The intensity data for the layers ($hk0 \longrightarrow hk3$) were collected on equi-inclination Weissenberg photographs by the multiple-film technique and were measured visually. The crystal ($0{\cdot}07 \times 0{\cdot}10$ mm. in cross-section) was mounted in a Lindeman glass capillary tube together with some of the solution from which it was grown. The measured intensities were corrected for Lorentz and polarisation factors by using a Cochran chart.[6]

In view of the large linear absorption coefficient, corrections for absorption were applied to the intensities by Lovell's method[7] which is based on that of Busing and Levy.[8] The values of the absorption correction, A, in the expression $I_{\text{corr.}} = AI_{\text{obs.}}$ ranged from 8·2 to 91·0. In spite of the large values of these absorption corrections, the corrected structure amplitudes agree well with those found for common reflections by Donohue and Helmholz who corrected their data for absorption by a different method (see Table 2).

Crystal Data.—Potassium silver carbonate: $KAgCO_3$; M, 207·0; $a = 20{\cdot}50 \pm 0{\cdot}20$, $b = 5{\cdot}82 \pm 0{\cdot}06$, $c = 6{\cdot}00 \pm 0{\cdot}06$ Å; $V = 716$ Å^3; $D_m = 3{\cdot}77$ g. cm.$^{-3}$; $Z = 8$; $D_c = 3{\cdot}94$ g. cm.$^{-3}$; $F(000) = 572$. Space group, *Ibca* (D_{2h}^{27}, no. 73). Absorption coefficient, $\mu = 580$ cm.$^{-1}$. Copper radiation, single-crystal oscillation and Weissenberg photographs.

Structure Determination.—For the space group, *Ibca*, there are 16 general equivalent positions:

$$(0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}) \pm (x, y, z;\ x, \bar{y}, \tfrac{1}{2} - z;\ \tfrac{1}{2} - x, y, \bar{z};\ \bar{x}, \tfrac{1}{2} - y, z).$$

As there are only eight potassium, eight silver, and eight carbon atoms in the unit cell they must be assigned to special positions. The twenty-four oxygen atoms in the unit cell may be distributed in a number of ways, but at least one set of eight must be in special positions.

As the reflections with $l = 2n + 1$ were exceedingly weak, Donohue and Helmholz concluded that the silver atoms were on two-fold axes parallel to c in special positions of the type $(0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}) \pm (0, \tfrac{1}{4}, z;\ \tfrac{1}{2}, \tfrac{3}{4}, z)$, as atoms in these special positions do not contribute to reflections with $l = 2n + 1$. Since some strong reflections with h and k odd were present, the possibility that the silver atoms were at centres of symmetry or on two-fold axes parallel to a or b was excluded. The positions of the potassium atoms were obtained from a Fourier projection ($hk0$) calculated by using the reflections whose signs were determined by the silver atom (with $z = 0{\cdot}128$). The potassium atoms were situated on the two-fold axes parallel to a in the special positions of the type $(0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}) \pm (x, 0, \tfrac{1}{4};\ x, \tfrac{1}{2}, \tfrac{3}{4})$, with $x = 0{\cdot}182$.

Those co-ordinates for silver and potassium, together with a temperature factor (with $B = 1{\cdot}5$ Å^2), were used to calculate a set of structure factors which were used to place the observed data from the four layers $hk0$, $hk1$, $hk2$, and $hk3$ on the same scale. The discrepancy factors (based on reflections to which the silver and potassium atoms contribute) for these layers were 0·20, 0·30, 0·39, and 0·41, respectively.

TABLE 1.

Final atomic parameters of potassium silver carbonate.

Atom	x/a	y/b	z/c	e.s.d. (Å) (r.m.s.)	B (Å^2)
K	−0·1815	0·0000	0·2500	0·011	1·5
Ag	0·0000	0·2500	0·1369	0·006	1·8
C	0·1282	0·0000	0·2500	0·043	2·6
O(1)	0·1888	0·0000	0·2500	0·035	2·5
O(2)	0·0962	0·1346	0·1074	0·043	2·5

The remaining atoms were located in a three-dimensional electron-density distribution. The carbon and a set of eight of the oxygen atoms were found to occupy special positions along the two-fold axes perpendicular to the (100) plane at approximately the same positions as found by Donohue and Helmholz. The remaining oxygen atoms were found to be situated in general positions; the x and the y co-ordinates agreed with those found by Donohue and Helmholz, but the z co-ordinates were different. In the first electron-density distribution, the electron

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[6] Cochran, *J. Sci. Instr.*, 1948, **25**, 397.

[7] Lovell, personal communication, 1961.

[8] Busing and Levy, *Acta Cryst.*, 1957, **10**, 180.

density at the position suggested by Donohue and Helmholz was small and negative, whereas that at the new position was approximately 4·4 eÅ^{-3} (this value rose to 8·3 eÅ^{-3} in the final cycle).

After four cycles of refinement by differential syntheses, the shifts in all the atoms were insignificant (less than 0·0005 Å). After each cycle the layers were rescaled by using $\Sigma|F_o| = \Sigma|F_c|$ as the criterion. Individual isotropic temperature factors were assigned to each atom by the method outlined by Cruickshank.[9] The co-ordinates obtained from the final cycle were corrected for termination-of-series errors by the back-shift method. The final atomic parameters are listed in Table 1; these gave an R factor of 0·18 for the observed reflections. The observed structure amplitudes and the calculated structure factors are listed in Table 2.

TABLE 2.

Calculated and observed structure factors for potassium silver carbonate.

(Scale: ½ absolute.)

h	F_c	F_o *	F_o †
	h, 0, 0		
4	100	110	101
6	182	175	109
8	89	109	73
10	188	142	138
12	135	112	113
14	49	56	62
16	107	89	105
18	64	64	76
20	57	58	66
22	86	75	98
24	34	39	51
26	33	31	
	h, 0, 2		
2	35	45	
6	−82	96	44
8	30	45	44
10	−35	44	33
12	−20	22	33
14	18	23	25
16	−48	43	44
20	10	11	
22	−28	30	
	h, 1, 1		
4	−47	30	44
6	35	30	44
8	28	39	51
10	−35	35	40
12	14	14	18
14	−1	4	
16	−17	13	22
18	22	18	25
	h, 1, 2		
1	−168	87	91
3	−131	79	131
5	−104	83	98
7	−111	102	95
9	−125	121	87
11	−117	97	73
13	−90	65	66
15	−70	55	62
19	−66	65	55
21	−60	59	40
23	48	45	33
	h, 1, 3		
2	−29	21	
4	14	17	
6	−11	13	
10	32	34	
12	−27	26	
14	−10	16	
16	17	20	
	h, 2, 0		
0	−61	75	58
2	−201	136	160
4	−157	116	116
6	−73	72	76
8	−170	122	127
10	−90	91	73
12	−93	102	91
14	−120	109	98
16	−43	50	50
18	−77	73	80
20	−77	80	76
22	−30	34	44
24	−55	47	51
	h, 2, 1		
1	−19	16	36
3	−30	25	47
7	22	22	36
9	16	19	33
11	−6	9	
13	−14	10	
15	−4	7	
17	7	7	
	h, 2, 2		
0	−56	60	69
2	61	58	51
4	35	36	25
6	−27	39	51
8	57	54	73
10	−6	12	
14	42	43	36
16	−19	29	25
18	17	19	
20	23	27	22
22	−13	15	18
	h, 2, 3		
1	6	5	
3	10	11	
7	−8	12	
9	−6	9	
	h, 3, 1		
2	26	26	44
4	−15	15	40
10	−31	31	62
12	26	18	29
14	9	9	
16	−17	23	
20	−10	7	15
	h, 3, 2		
1	95	84	69
3	108	94	83
5	113	99	102
7	100	82	87
9	82	76	80
11	73	70	69
13	74	73	73
15	73	78	83
17	62	63	62
19	50	50	51
21	42	42	
	h, 3, 3		
4	30	22	
6	−21	18	
8	−19	20	
10	21	17	
12	9	7	
	h, 4, 0		
0	128	110	123
2	61	64	62
4	98	101	106
6	139	127	112
8	52	70	69
10	81	84	131
12	72	86	91
14	48	82	87
16	92	121	106
18	47	60	62
20	27	28	29
	h, 4, 2		
0	−61	59	58
2	12	20	25
6	−39	44	36
8	16	25	
10	81	84	18
12	−17	29	
14	15	27	33
16	−29	38	33
	h, 5, 1		
2	14	13	15
4	−15	14	15
6	11	14	15
8	3	7	
10	−21	18	36
12	17	25	29
14	3	16	
	h, 5, 2		
1	−61	71	58
3	−72	78	69
5	−77	86	58
7	−68	79	58
9	−54	65	51
11	−49	49	44
13	−52	69	55
15	−52	53	44
17	−45	37	
	h, 5, 3		
4	19	10	
6	−13	11	
8	9	11	
10	17	20	
12	−10	4	
	h, 6, 0		
0	−27	34	
2	−75	90	91
4	−67	77	83
6	−39	46	47
8	−73	84	83
10	−38	43	55
12	−41	47	65
14	−61	50	73
	h, 6, 2		
0	−18	39	25
2	24	38	29
4	13	22	
6	−11	20	15
8	25	34	18
	h, 7, 2		
1	43	35	
3	41	50	

* Present work. † Ref. 1

Reflections for which $h = 2n + 1$, $k = 2n$, and $l = 2n + 1$ have contributions from the set of oxygen atoms in general positions only. The R factor for these reflections, 0·20 from the final co-ordinates, should be compared with a value of 0·30 from the co-ordinates given by Donohue and Helmholz.

Scattering factors for carbon, oxygen, and potassium were those of Berghius *et al.*[10] and for silver that given by Thomas and Umeda.[11] Calculations of structure factors, electron density

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[9] Cruickshank, *Acta Cryst.*, 1956, **9**, 747.

[10] Berghuis, Haanappel, Potters, Loopstra, McGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

[11] Thomas and Umeda, *J. Chem. Phys.*, 1957, **26**, 293.

distributions, and differential syntheses were carried out on UTECOM (a Deuce electronic digital computer) with programmes written by Dr. J. S. Rollett and one of us (G. A. B.).

Description of Structure

Crystals of potassium silver carbonate consist of infinite chains of silver atoms bridged by carbonate groups. The chains are held together by discrete potassium ions. The atomic arrangement within the unit cell is shown in Fig. 1.

The silver atoms form a continuous row along each two-fold axis parallel to *c*. The repeating distance between each silver atom is *c*/2 (*i.e.*, 3·00 Å) which closely approaches the silver–silver distance in metallic silver (2·89 Å) [12] and in silver perfluorobutyrate (2·90 Å).[13]

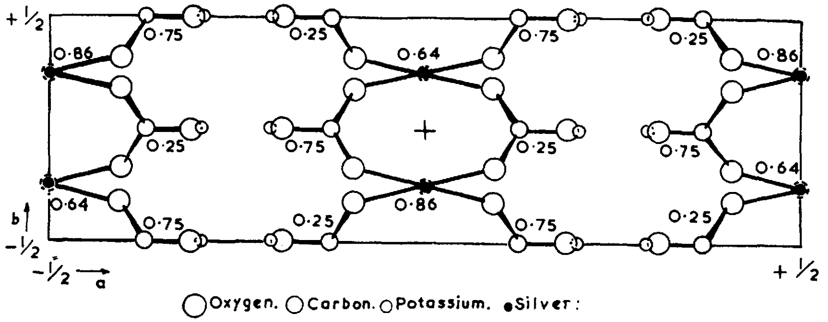

FIG. 1. Arrangement of the atoms in the unit cell of potassium silver carbonate. The broken circle about each silver atom denotes another silver atom underneath it. These atoms are separated by *c*/2. The fractional *z*-co-ordinates of the carbon and the top silver atoms are shown.

Each silver atom, which has an almost linear co-ordination, is bonded to two oxygen atoms from different carbonate groups; the angle O–Ag–O is 170°. Each carbonate group bridges two silver atoms which are situated on neighbouring two-fold axes and are separated by *b*/2, with the result that there are infinite zig-zag chains of carbonate-bridged silver atoms parallel to *b*; the angle C–O–Ag is 125°. The distance between bridged silver atoms is 3·21 Å. Besides the two close silver–silver distances already mentioned (3·00 and 3·21 Å), there is a third at 3·34 Å.

The chains of carbonate-bridged silver atoms are held together by the potassium ions, which are situated along two-fold axes parallel to *a*. Each potassium ion has a total of nine contacts with oxygen atoms from five separate carbonate groups. One contact at 2·66 Å is to the O(1) atom of a carbonate group whose centre is along the same two-fold axis as the potassium ion. The other four carbonate groups have each two contacts. The two-fold axes containing the centres of two of these four carbonate groups are on either side of that containing the potassium ion and are at a distance of *b*/2 from it; all three axes are contained in a plane parallel to (001). The other two carbonate groups are similarly situated along two-fold axes parallel to that which contains the potassium ion; these three axes are contained in a plane parallel to (010) and the distance between each axis is *c*/2. There are four distinct distances, two to the O(1) atoms at 2·92 Å and 3·01 Å in the planes parallel to *b* and *c*, respectively, and two at 2·87 and 2·88 Å to O(2) atoms of the two respective carbonate groups. The five O(1) atoms involved in the contacts form a slightly distorted square-pyramidal arrangement about the potassium ion, and the contacts from the O(2) atoms are on that side of the base which is opposite to the apex.

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[12] Pearson, " Lattice Spacings and Structures of Metals and Alloys," Pergamon, London, 1957.
[13] Blakeslee and Hoard, *J. Amer. Chem. Soc.*, 1956, **78**, 3029.

The bond distances and angles of the carbonate complex are shown in Fig. 2 and are listed together with their estimated standard deviations in Table 3. Although the estimated standard deviations are large, the carbon–oxygen distances (1·24, 1·33 Å) agree well with those observed in carbonatotetra-amminecobalt(III) bromide[14] (1·24, 1·34 Å) and calcite[15] (1·29 Å): the bond angles are very close to 120°. Because one of the oxygen atoms and the carbon atom of the carbonate group are on a two-fold axis, the carbonate group must be planar.

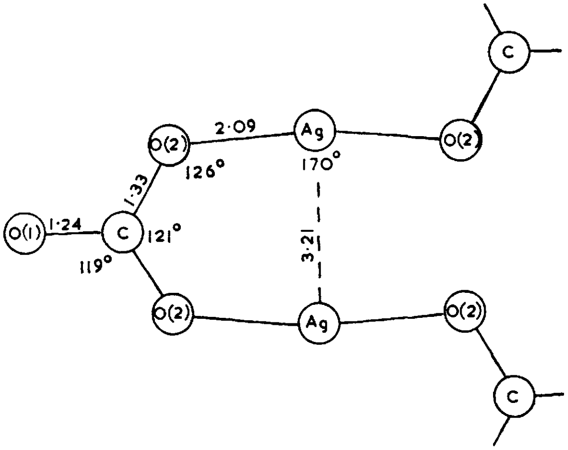

FIG. 2. Bond distances (Å) and angles in potassium silver carbonate.

TABLE 3.

Interatomic dimensions in potassium silver carbonate.

Bond	Length (Å)	e.s.d. (Å)	Angle	Value	e.s.d.
Ag–O(2)	2·09	0·043	O(2)–Ag–O(2)	170·0°	1·5°
C–O(2)	1·33	0·065	Ag–O(2)–C	126·5	1·5
C–O(1)	1·24	0·060	O(2)–C–O(2)	121·0	1·5
			O(1)–C–O(2)	119·5	1·5

While there is a considerable scatter of the silver–oxygen distances reported in the literature, the silver–oxygen distance found in potassium silver carbonate compares favourably with recent determinations of this distance (see Table 4).

TABLE 4.

Silver–oxygen distances (Å).

$KAgCO_3$	$AgO_2C{\cdot}C_3F_7$ [13]	$Ag_2C_2O_4$ [16]	Ag_2O [3]	Ag_2SO_4 [17]	Ag_3AsO_4 [17]	Ag_3PO_4 [18]	$AgClO_4$ [19]	Ag_2CO_3 [1]
2·09	2·25	2·17—2·30	2·05	2·50	2·34	2·34	2·51	2·30

The close silver–silver distances in potassium silver carbonate are comparable with the silver–silver distance in metallic silver, and hence the possibility of bonding between these atoms cannot be ignored. Since the silver(I) atom has a closed (d^{10}) configuration there would be no expected difference in the magnetic properties of this compound, so that independent evidence of silver–silver bonding [of the type obtained for copper–copper bonding in copper(II) compounds] is not possible.

Barclay and Hoskins[14] suggested that, in view of the close geometrical resemblance of the carbonate to the carboxylate group, the co-ordinating behaviour of the former should parallel that of the latter. In potassium silver carbonate each carbonate group

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[14] Barclay and Hoskins, *J.*, 1962, 586.
[15] Sass, Vidale, and Donohue, *Acta Cryst.*, 1957, **10**, 567.
[16] Griffith, *J. Chem. Phys.*, 1943, **11**, 499.
[17] Helmholtz and Levine, *J. Amer. Chem. Soc.*, 1942, **64**, 354.
[18] Helmholtz, *J. Chem. Phys.*, 1936, **4**, 316.
[19] Náray-Szabó and Pócza, *Z. Krist.*, 1942, **104**, 28.

bridges two silver atoms in a *syn-syn*-conformation in a similar fashion to the carboxylate group in copper(II) acetate monohydrate.[20]

Although this structure differs from that found by Donohue and Helmholz only in the position of one oxygen atom, the stereochemistry of the silver atom is different and the structure is more chemically feasible. The silver atom has essentially linear co-ordination found in many compounds of univalent silver.

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[20] van Niekerk and Schoening, *Acta Cryst.*, 1953, **6**, 227; Martin and Waterman, *J.*, 1959, 1359.