sodium sulfate.[10] Thus, in these two instances, the effect on the entropy of removing one oxygen atom from a sulfate group to form a sulfite group is a decrease of about 1 unit. A difference of this order of magnitude reasonably may be expected between sulfates and sulfites of other metals, and this offers a means of estimating the entropy of the sulfite when that of the sulfate is known or *vice versa.*

The entropy of manganese dithionate-dihydrate may be subject to some correction because of unextracted magnetic entropy; but sufficient information on this point is not available at present, and it is not taken account of in the error assigned to the entropy value in Table II. In view of recent observations[11] on the approximate constancy of the entropy of water of crystallization, one would estimate the entropy of anhydrous manganese dithionate to be about 45 units at 298.16°K. and that of the hexahydrate to be about 110 units.

Summary

Low-temperature specific heat measurements, throughout the temperature range 51 to 298°K., have been made of calcium sulfite, sodium sulfite, and manganese dithionate-dihydrate.

The respective entropies at 298.16°K. are 24.2 ± 0.3, 34.9 ± 0.4, and 66.7 ± 1.0.

It is suggested that the difference in entropy between a sulfate and a sulfite group in a solid compound is about 1 unit at 298.16°K.

BERKELEY, CALIF. RECEIVED OCTOBER 25, 1943

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[10] Pitzer and Coulter, THIS JOURNAL, **60**, 1310 (1938).

[11] Kelley and Moore, *ibid.*, **65**, 2340 (1943).

[CONTRIBUTION FROM STEELE CHEMICAL LABORATORY, DARTMOUTH COLLEGE]

The Crystal Structure of Potassium Silver Carbonate, $KAgCO_3$[1]

BY JERRY DONOHUE[2] AND LINDSAY HELMHOLZ

Introduction.—The determination of the structure of potassium silver carbonate, which is colorless, was undertaken in conjunction with that of silver carbonate,[3] which is yellow, for the purpose of establishing the character of the silver-oxygen bond in those crystals, and discussing the difference in color in terms of the rule suggested by Pitzer and Hildebrand,[4] which states that the color of a compound formed from colorless ions is related to the amount of "covalent character" in the bond between these ions. Since the electronic structure of the carbonate group can readily be interpreted in terms of single bond double bond resonance, any effect of silver to oxygen covalent bond formation on the normal ionic configuration could be discussed in a relatively straightforward manner. Unfortunately an accurate structure of silver carbonate, in which appreciable covalent bond formation is suggested both by approximate distances and the rule of Pitzer and Hildebrand, is not yet available.

Experimental.—Potassium silver carbonate was prepared by the method of de Schulten.[5] Silver nitrate solution (0.25 *m*) was added dropwise to 50% potassium carbonate saturated with potassium bicarbonate. The yellow precipitate first formed turned white on standing. Complete solution takes place on heating. Slow cooling of this hot solution in a Dewar flask gives needle-like crystals, elongated in the *c* direction. The crystals prepared in this manner had all the properties described by de Schulten. Goniometric examination showed the crystals to be possibly orthorhombic, there being well-developed (100) and (110) faces ($a:b = 3.54:1$). Laue photographs showed the Laue symmetry D_{2h}-mmm, this establishing the orthorhombic symmetry.

Oscillation photographs were taken with the *c* axis vertical, using CuKα radiation. One oscillation photograph using Mo Kα radiation was taken for the purpose of obtaining more layer lines. The dimensions of the unit cell, as determined by indexing those photographs, were found to be $a_0 = 20.23$ Å., $b_0 = 5.75$ Å., $c_0 = 5.95$ Å. (all ±0.5%) ($a:b:c = 3.521:1:1.036$). Indexing of symmetric and asymmetric Laue photographs ($\lambda_{\text{min.}} = 0.24$ Å.) showed no first order reflections requiring a larger unit cell.

The number of molecules in the unit cell (using de Schulten's density value of 3.77 g./cc.) is calculated to be 7.66. Assumption of eight molecules in the unit cell gives a calculated density of 3.94 g./cc. de Schulten's value is low probably due to the fact that potassium carbonate clings tenaciously to the surface of the crystals as prepared. Attempts to measure the density also gave low values.

The intensities of the reflections on the oscillation photographs were estimated by means of the multiple film technique,[6] and by taking pictures of different exposure times over the same range. It was found necessary to correct the intensities for absorption; the correction factor was derived by integrating the expression for the path of beam through the crystal (assumed to be bathed by the beam) in accordance with the relation $I = I_0K|F|^2 e^{-\mu p}\,dp$ where I = the corrected intensity, I_0 = the incident intensity, K = the product of the Lorentz, polarization and temperature factors, F = the structure factor, μ = the absorption coefficient, and P = the path length of the beam through the crystal. The path length is expressed as function of: A, the width of the crystal; α, the angle through which the crystal has been rotated; and φ, the azimuthal scattering angle. Two cases are considered: (1) the incident and the emergent rays pass through the same crystal face, and (2) these two rays pass through different crystal faces. For case (1), the simplified expression is $I = I_0K|F|^2 \dfrac{A \sin\alpha}{\mu c}$, where $c = 1 + \dfrac{\sin\alpha}{\sin(\alpha - \varphi)}$. For case (2), the simplified expression is $I = I_0K|F|^2 \left(\dfrac{\sin(2\alpha - \varphi)}{\mu^2}\right)$. In

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[1] Abstracted from a thesis submitted by Jerry Donohue to Dartmouth College in partial fulfillment of the requirements for the degree of Master of Arts.

[2] Present address: Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California.

[3] John E. Eldridge, Thesis, 1943, Dartmouth College.

[4] K. S. Pitzer and J. H. Hildebrand, THIS JOURNAL, **63**, 2472 (1941).

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

[6] J. J. de Lange, J. M. Robertson and I. Woodward, *Proc. Roy. Soc.* (London), **A171**, 398 (1939).

simplifying the integrated expressions, certain terms were found to be negligible because of the large value of μ (575).

The validity of the correction factors was checked by calculating the F values of certain reflections which appear when the crystal has been rotated through different angles, and hence appear on different films with different intensities. Some of these comparisons are shown in Table I.

TABLE I

(*hkl*)	Observed intensity	α	F, corrected
(132)	2.50	30°	20
	1.40	41°	18
(532)	4.15	12°	32
	1.50	63°	25
(752)	2.50	33°	17
	1.45	77°	16

Determination of the Structure.—The following regular absences, observed on the oscillation photographs: (hkl) with $h + k + l \neq 2n$, ($hk0$) with $h \neq 2n$ and $k \neq 2n$, ($h0l$) with $h \neq 2n$ and $l \neq 2n$, and ($0kl$) with $k \neq 2n$ and $l \neq 2n$, establish the space group uniquely as $D_{2h}^{27} - Ibca$.[7] The sets of positions for the space group $D_{2h}^{27} - Ibca$ are[7]

$$
\begin{array}{lllllllllllllll}
\multicolumn{15}{l}{(0\ \ 0\ \ 0;\ \tfrac12\ \ \tfrac12\ \ \tfrac12)\ +} \\
8: & (a) & 0 & 0 & 0; & 0 & \tfrac12 & \tfrac12; & \tfrac12 & 0 & \tfrac12; & \tfrac12 & \tfrac12 & 0 \\
 & (b) & \tfrac14 & \tfrac14 & \tfrac14; & \tfrac14 & \tfrac34 & \tfrac34; & \tfrac34 & \tfrac14 & \tfrac34; & \tfrac34 & \tfrac34 & \tfrac14 \\
 & (c) & x & 0 & \tfrac14; & \bar{x} & 0 & \tfrac34; & x & \tfrac12 & \tfrac34; & \bar{x} & \tfrac12 & \tfrac14 \\
 & (d) & \tfrac14 & y & 0; & \tfrac34 & \bar{y} & 0; & \tfrac34 & y & \tfrac12; & \tfrac14 & \bar{y} & \tfrac12 \\
 & (e) & 0 & \tfrac14 & z; & 0 & \tfrac34 & \bar{z}; & \tfrac12 & \tfrac34 & z; & \tfrac12 & \tfrac14 & \bar{z} \\
16: & (f) & \multicolumn{12}{l}{x\ \ y\ \ z;\ x\ \ \bar{y}\ \ \tfrac12\ \ z;\ \tfrac12 - x, y, \bar{z};\ \bar{x}, \tfrac12 - y, z;} \\
 & & \multicolumn{12}{l}{\bar{x}\ \ \bar{y}\ \ \bar{z};\ \bar{x}, y, \tfrac12 + z;\ \tfrac12 + x, \bar{y}, z;\ x, \tfrac12 + y, \bar{z}.}
\end{array}
$$

Into a unit cell of such a spatial symmetry must be placed 8 silver atoms, 8 potassium atoms, 8 carbon atoms, and 24 oxygen atoms.

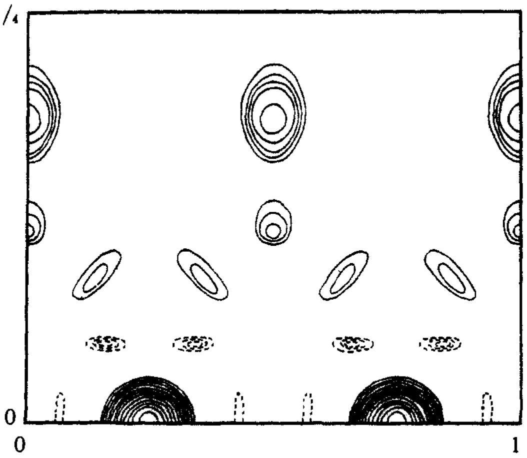

Fig. 1.—(x, y). Projection of electron density of 1/4 of the unit cell on (001). Contours are drawn at 12.5, 25, 37.5, 50, and at 100 to 800 in 100 unit intervals, in terms of an arbitrary scale.

The silver atoms must be assigned to the position 8(e) to account for the fact that reflections for which $l \neq 2n$ are exceedingly weak compared to those for which $l = 2n$. Positions 8(a) and 8(b) are excluded by the presence of strong reflections with h or k odd. With the silver atoms assigned to the positions 8(e), the signs of all the F_{hk0}'s can be determined. A Fourier projection on the xy plane made by using the 42 available ($hk0$) reflections is shown in Fig. 1. The peaks at $x = 0, y = \frac14$ and $x = 0, y = \frac34$ are clearly those of the silver atoms. The next largest peak at $x \approx 0.185, y = \frac12$ is due to the potassium atom superimposed on one oxygen atom of the carbonate group. The remainder of the carbonate group is also clearly shown. The peaks drawn in with dotted contours are believed to be spurious. No reasonable interpretation could be given to any of these spurious peaks. The Fourier projection places the potassium atoms, the carbon atoms, and eight oxygen atoms in the positions 8(c); the remaining sixteen oxygen atoms must fall into the general positions 16(f). There are thus in all seven parameters to be determined.

As a start in the parameter determination, the carbonate group was assumed to have the same configuration and dimensions as in calcite.[8] The intensities of the ($h00$) reflections can thus be considered to be functions of two variables: the x parameter for the potassium atom, and the x parameter for the carbonate group. Using the eleven available ($h00$) reflections, limits for these parameters were obtained by calculating and comparing F values in the usual way. Atomic scattering factors taken from the tables of Pauling and Sherman,[9] and a temperature factor with $\beta = 1.5$ were used in these calculations.

Using these x parameters, the z parameters for the silver atoms and the oxygen atoms in the general positions (O_{II}) can now be obtained in the same way from F values of (hkl) reflections. If $z_{O_{II}} = z_{Ag} + 0.250$ the silver atom is bisphenoidally surrounded by four oxygen atoms. Any other arrangement is chemically unreasonable, unless the silver atom is two coördinated, and this structure leads to improbable interatomic distances. The F values of the reflections of the type $h \neq 2n, k \neq 2n, l = 2$ were found to be very sensitive to small changes in the silver parameter, since its value is very close to $\frac18$. The y parameter of O_{II} can now be calculated, because of the assumption made concerning the configuration and dimensions of the carbonate group. A check on the parameters of O_{II} is found in the F values for reflections of the type $h \neq 2n, k = 2n, l \neq 2n$, since none of the other atoms in the cell contribute to these reflections.

The final parameter values are

K $x = -0.182$
C $x = .122$
O $x = .187$
Ag $z = .128$
O_{II} $x = .089$ $y = 0.146$ $z = 0.378$

We believe it unlikely that any of the potassium

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(7) "International Tables for the Determination of Crystal Structures," Vol. I.

(8) N. Elliott, THIS JOURNAL, **59**, 1380 (1937).

(9) L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

TABLE II

VALUES OF $F_{(hkl)}$

hkl	$F_{obs.}$	$\lvert F\rvert_{calcd.}$	hkl	$F_{obs.}$	$\lvert F\rvert_{calcd.}$	hkl	$F_{obs.}$	$\lvert F\rvert_{calcd.}$
200	[a]		121	10	4	022	19	17
400	28	24	321	13	8	222	14	11
600	30	41	521	abs.	2	422	7	5
800	20	16	721	10	6	622	14	10
10.0.0	38	44	921	9	5	822	20	15
12.0.0	31	34	11.2.1	abs.	1	10.2.2	abs.	5
14.0.0	17	12	13.2.1	abs.	3	12.2.2	abs.	1
16.0.0	29	26	231	12	7	14.2.2	10	10
18.0.0	21	14	431	11	10	16.2.2	7	8
20.0.0	18	14	631	abs.	3	18.2.2	abs.	2
22.0.0	27	28	831	abs.	1	20.2.2	6	5
24.0.0	14	12	10.3.1	17	9	22.2.2	5	6
020	16	14	12.3.1	8	6	132	19	22
220	44	48	14.3.1	abs.	4	333	23	24
420	32	36	16.3.1	abs.	2	532	28	26
620	21	15	18.3.1	abs.	2	732	24	24
820	35	39	20.3.1	4	5	932	22	20
10.2.0	20	20	141	abs.	2	11.3.2	19	18
12.2.0	25	22	341	abs.	3	13.3.2	20	19
14.2.0	27	30	541	abs.	1	15.3.2	23	18
16.2.0	14	11	741	abs.	3	17.3.2	17	18
18.2.0	22	19	941	abs.	3	19.3.2	14	16
20.2.0	21	22	11.4.1	abs.	0	042	16	13
22.2.0	12	9	251	4	2	242	7	6
24.2.0	14	18	451	4	5	442	abs.	2
040	34	30	651	4	4	642	10	8
240	17	13	851	abs.	2	842	0	9
440	29	22	10.5.1	10	6	10.4.2	5	5
640	31	34	12.5.1	8	4	12.4.2	abs.	2
840	19	13	14.5.1	abs.	0	14.4.2	9	8
10.4.0	36	21	16.5.1	5	3	16.4.2	9	8
12.4.0	25	17	18.5.1	5	3	18.4.2	abs.	0
14.4.0	24	10	202	[a]		20.4.2	abs.	4
16.4.0	29	26	402	abs.	4	152	16	21
18.4.0	17	16	602	12	14	352	19	17
20.4.0	8	8	802	12	11	552	16	14
060	abs.	5	10.0.2	9	8	752	16	15
260	25	20	12.0.2	9	2	952	14	18
460	23	19	14.0.2	7	9	11.5.2	12	19
660	13	12	16.0.2	12	10	13.5.2	15	16
860	23	22	18.0.2	abs.	1	15.5.2	12	13
10.6.0	15	10	20.0.2	abs.	4	062	7	8
12.6.0	18	11	22.0.2	7	7	262	8	5
14.6.0	20	20	112	25	25	462	abs.	2
211	abs.	3	312	36	33	662	4	5
411	12	12	512	27	37	862	5	8
611	12	9	712	26	32	10.6.2	abs.	3
811	14	8	912	24	24	12.6.2	abs.	0
10.1.1	11	7	11.1.2	20	18			
12.1.1	5	3	13.1.2	18	19			
14.1.1	abs.	1	15.1.2	17	22			
16.1.1	6	4	17.1.2	16	21			
18.1.1	7	5	19.1.2	15	18			
20.1.1	abs.	1	21.1.2	11	14			
22.1.1	abs.	0	23.1.2	9	12			
24.1.1	5	3						

[a] Not observed because of experimental arrangement.

or silver parameters are in error by as much as ±0.002, since variation of this magnitude leads to serious discrepancies between observed and calculated F values. The oxygen and carbon parameters may be in error by more than this amount if there is a distortion from the assumed configuration of the carbonate group. However, a big distortion is rather unlikely.

Calculated and observed F values are shown in Table II.

Discussion

A projection of a portion of the unit cell on (100) is shown in Fig. 2. The silver atoms are surrounded by four oxygen atoms at 2.42 ± 0.05 Å. The potassium atom has nine close oxygen neighbors, one at 2.65 ± 0.08 Å., and four each at 2.88 Å. and 3.00 Å. all ±0.05 Å. The shortest potassium to oxygen distance is the only coördination the potassium atom has in that direction.

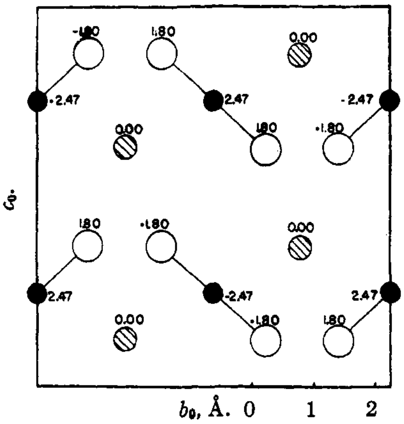

Fig. 2.—Projection of a portion of the unit cell on (100). Numbers give heights of atoms in Å. above plane of diagram ($x = {}^1/_2$). Black circles represent carbon atoms, open circles, oxygen atoms and shaded circles, silver atoms. In this projection, the positions of the potassium atoms coincide with those of the carbon atoms.

The oxygen atoms in the positions 8(c) are octahedrally coördinated; in addition to being bonded to the carbon atom in the carbonate group, they are surrounded by five potassium atoms (one at 2.65 Å., two each at 2.88 Å. and 3.00 Å.) in such a way as to form a deformed octahedron. The oxygen atoms in the general positions have a more nearly triangular coördination, being close to two silver atoms (at 2.42 Å.), in addition to the carbonate group bond. Their next nearest neighbor is a potassium atom, at 2.88 Å.

Although we have made an assumption concerning the internal structure of the carbonate group, we feel that any significant deviation from the normal configuration would have been detected. Since the X-ray data indicate that such deviation is unlikely, it is probable that the carbonate group has its usual structure[8] in this crystal.

It is seen that the carbonate groups are tipped about 42° out of a plane parallel to (001). The binding between the silver atoms and the oxygen atoms is staggered in such a way that there are strong forces in both the *b* and *c* directions. This is in agreement with the observed growth of the crystals.

A preliminary report on the structure of silver carbonate[9] follows: Laue and rotation pictures showed the crystals to be monoclinic with a_0 = 4.83 Å., b_0 = 9.52 Å., c_0 = 3.23 Å., β = 92.7°, z = 2 (calcd. 1.99). The probable space group is C_2^2-$P2_1$. Patterson and Fourier analysis of (*hk*0) data gives positions for the silver atoms and probable positions for the carbonate groups. The silver atoms are surrounded by deformed tetrahedra of oxygen atoms at about 2.3 Å. The binding is somewhat similar to that in potassium silver carbonate, there being a staggered arrangement of bonds between the silver and oxygen atoms.

The table given by Helmholz and Levine[10] can now be extended:

TABLE III

Compound	Ag-O,[a] Å.	Radius Sums Ionic	Radius Sums Covalent	Color
$AgClO_3$[11]	2.51	2.46	2.19	Colorless
Ag_2SO_4	2.50	2.46	2.19	Colorless
$KAgCO_3$	2.42	2.46	2.19	Colorless
Ag_3PO_4	2.34	2.46	2.19	Yellow
Ag_3ASO_4	2.34	2.46	2.19	Deep red
Ag_2CO_3	2.30	2.46	2.19	Yellow
Ag_2O	2.06		2.02	Brown-black

[a] Average distance.

The correlation between the color and the bond distance is in reasonable accord with the rule of Pitzer and Hildebrand.[4] In view of the nature of the absorption process,[12] it seems probable that the *change* in absorption when, for example, silver is substituted for sodium in salts of these acids, rather than the color of the silver salt itself, should serve as a criterion for the amount of covalent character, in crystals of the type considered here. The apparent discrepancies in Table III of potassium silver carbonate and silver arsenate can be explained on this basis, and would lead, in the case of silver arsenate, to the reasonable conclusion that the tendency of the arsenate group to share electrons is greater than that of the phosphate group.

Summary

The crystal structure of potassium silver carbonate has been determined. The crystal is orthorhombic holohedral, with a_0 = 20.23 Å., b_0 = 5.75 Å., c_0 = 5.95 Å. The space group is D_{2h}^{27}-*Ibca*. The Ag-O bond distance was found to be 2.42 Å., and this is discussed in relation to other silver salts, including silver carbonate, for which a preliminary structure is given. The application of the rule of Pitzer and Hildebrand to the probable nature of this bond is also discussed.

PASADENA, CALIF. RECEIVED OCTOBER 11, 1943

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[10] L. Helmholz and R. Levine, THIS JOURNAL, **64**, 354 (1942).

[11] I. Naray-Szabo and J. Pocza, *Z. Krist.*, **104**, 28 (1942).

[12] G. K. Rollefson and M. Burton, "Photochemistry and the Mechanism of Chemical Reactions," Prentice Hall, New York, N. Y., 1939, Chapter VI.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MISSOURI]

Normal and Pseudo Structures of 8-Benzoyl-1-naphthoic Acid and Derivatives[1,2]

BY H. E. FRENCH AND J. E. KIRCHER

An earlier paper from this Laboratory[3] gave evidence for both the symmetrical and the unsymmetrical forms for 1,8-naphthalyl dichloride. This work has now been extended to the 8-benzoyl-1-naphthoic acid and certain of its derivatives.

8-Benzoyl-1-naphthoic Acid.—This acid was prepared by the method of Mason.[4] Upon crystallization from ethanol, 70% acetic acid, or chloroform, we obtained a product melting at 110°, as reported by Mason. From xylene, cyclohexane or toluene, the substance melted at 129–130°, checking the melting point reported by Knapp.[5] A sample of the 110° melting material heated to 90° for four hours under a watch glass was found to melt at 154°. From all of these samples, material of melting point 110° or 129–130° could be obtained by crystallization from the proper solvent.

Absorption curves were plotted for the acids melting at 110° and 129°, in chloroform solution, and for the 129° variety after refluxing in cyclohexane solution for twenty-four hours. The curves were all of the same form, with maximum and minimum points in the same regions. These maximum and minimum points are given in Table I. These curves for the acid are similar to the curve for diphenylnaphthalide, and bear no resemblance to the curve for dibenzoylnaphthalene which shows only one minimum and one maximum. Data for these curves are also given in Table I.[6]

Diphenylnaphthalide, ditolylnaphthalide and naphthalic anhydride, all of which have a ring structure across the 1,8 positions, were found to

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[1] This paper is a summary of part of the thesis material submitted by Dr. Kircher to the graduate faculty of the University of Missouri.

[2] The material in this paper was presented at the meeting of the American Chemical Society at Detroit, Mich., in April, 1943.

[3] French and Kircher, THIS JOURNAL, **63**, 3270 (1941).

[4] Mason, *J. Chem. Soc.*, **125**, 2116, 2119 (1924).

[5] Knapp, *Monatsh.*, **67**, 332 (1936).

[6] The spectroscopic data were determined by Dr. Victor Ells, University Spectroscopist for the University of Missouri.