

The Structure of the $(\text{HCO}_3)_2^-$ Ion in Potassium Bicarbonate

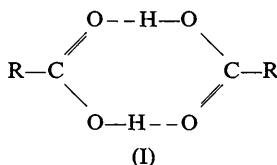
BY BJØRN PEDERSEN

Sentralinstitutt for industriell forskning, Oslo 3, Norway

(Received 23 June 1967)

From the nuclear magnetic resonance spectrum of KHCO_3 powder it is found that the proton-proton distance in the ion $(\text{HCO}_3)_2^-$ is $2.274 \pm 0.006 \text{ \AA}$, which is significantly larger than the calculated distance assuming a planar ion, 2.14 \AA . The existing literature data are discussed in the light of this result.

Several carboxylic acids are known to crystallize in the dimer form (I).



It is generally found that the dimers are planar (Robertson, 1964). However, a simple calculation based on expected interatomic distances and angles in such a dimer shows that the two H atoms will approach about 0.3 \AA closer than the van der Waals distance, raising the question of whether the H atoms will be located in the plane of the other atoms. To throw some light on this question we have studied potassium bicarbonate, where the HCO_3^- ions form dimers of the type (I), with proton magnetic resonance methods.

The crystal structure of potassium bicarbonate has been determined from X-ray diffraction data by Herpin (1952) and Nitta, Tomiie & Koo (1952, 1954), but the two sets of atomic positions determined are not in good agreement. Herpin & Meriel (1964) have recently located the hydrogen atoms, and carried out a least-squares refinement, on the basis of $hk0$ neutron diffraction data. Herpin & Meriel (1964) give interatomic distances in their paper, but it is not clear which z coordinates they have used in the calculation of these distances. We will assume the z coordinates earlier found by Herpin (1952) for the heavier atoms and as a first approximation the z coordinate for the H atom obtained by placing the H atom in the plane determined by the other atoms in the carbonate ion to which it is bound. These coordinates are given in Table 1.

Table 1. *The positional parameters in KHCO_3 as fractions of the cell edges*

	x	y	z
K	0.167	0.025	0.300
O(1)	0.194	0.530	0.090
O(2)	0.082	0.321	-0.285
O(3)	0.076	0.719	-0.285
C	0.119	0.517	-0.160
H	0.013	0.687	-0.492

If we use the coordinates given in Table 1, we get interatomic distances which are not in complete agreement with the values given by Herpin & Meriel (1964). We have therefore given the dimensions of the bicarbonate ion in Fig. 1. These dimensions are in very good agreement with the corresponding dimensions of the bicarbonate ion in sodium bicarbonate found by Sass & Scheuerman (1962), illustrated in their Fig. 4.

The three O-O distances in the ion in KHCO_3 are found to be equal to 2.243 \AA (within 0.001 \AA), indicating that the opening of the O(1)-C-O(2) angle is coupled to the lengthening of the C-O(3) bond. No effect from the hydrogen bond formation can be found in the carbon-oxygen acceptor [C-O(2)] bond either in the potassium or in the sodium salt.

The H atom is found to be at a distance of 1.081 \AA from O(3), and the angle C-O(3)-H is 111.9° using the coordinates in Table 1. The H-H distance is 2.14 \AA , which is, as pointed out above, smaller than the van der Waals distance, 2.4 \AA .

To get additional information on the location of the H atoms, we have studied the proton magnetic resonance spectrum of potassium bicarbonate in powder form. The protons in KHCO_3 are distributed in fairly isolated H-H pairs in the lattice, where each $(\text{HCO}_3)_2^-$ ion constitutes a pair. We have therefore fitted a theoretical pair-powder spectrum to the experimentally

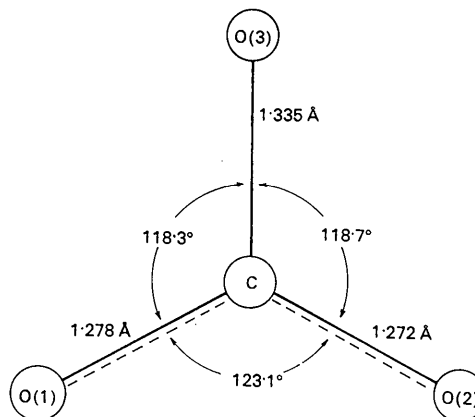


Fig. 1. The bicarbonate ion in KHCO_3 .

obtained spectrum by least-squares methods, as discussed in detail elsewhere (Pedersen, 1968).

The calculated and observed spectrum are in good agreement, as shown in Fig. 2. Interestingly enough, the pair-powder spectrum of KHCO_3 is very similar to the nuclear magnetic resonance spectrum of potassium oxalate monoperhydrate, $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$ [$=(\text{KHCO}_3)_2$], where the protons are paired in H_2O_2 molecules (Pedersen & Pedersen, 1967).

The pair-powder spectrum depends on only two factors of physical significance, α and β^2 . The mean values of these quantities obtained from the analysis of five spectra are:

$$\alpha = 1.800 \pm 0.014 \text{ G} \quad \text{and} \quad \beta^2 = 0.53 \pm 0.02 \text{ G}^2.$$

α has earlier been determined by Kume & Kakiuchi (1960) from a single-crystal nuclear magnetic resonance study, and their result, $1.81 \pm 0.1 \text{ G}$, is in excellent agreement with our value.

The quantities α and β^2 are related to the structure through the following equations:

$$\alpha = 3\mu/2R^3 \quad (1)$$

$$\beta^2 = M_{2e}, \quad (2)$$

where R is the proton-proton distance in the $(\text{HCO}_3)_2^-$ ion, μ the magnetic dipole moment of a proton ($14.1042 \text{ G } \text{\AA}^3$), and M_{2e} the *inter-pair* contribution to the van Vleck second moment (Pedersen, 1968).

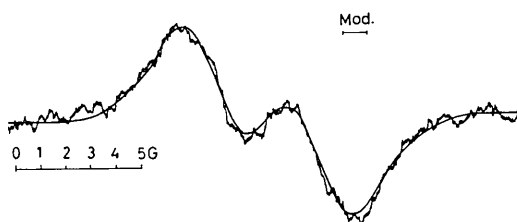


Fig. 2. The proton magnetic resonance spectrum of potassium bicarbonate powder. The smooth curve represents a theoretical spectrum fitted to the experimental spectrum. The modulation amplitude (peak-peak) used is shown in the upper right.

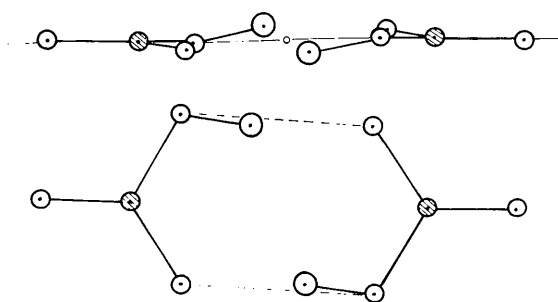


Fig. 3. The $(\text{HCO}_3)_2^{2-}$ ion in potassium bicarbonate as seen along the b axis (above) and normal to the b axis (below). The centre of symmetry of the molecule is indicated.

From equation (1) and the value we have found for α , the value of the pair distance is found to be

$$R = 2.274 \pm 0.006 \text{ \AA},$$

which is significantly larger than the value found by placing the H atom in the plane of the carbonate ion, 2.14 \AA . Hence, we must conclude that the H atoms are not in the plane determined by the two carbonate ions, but somewhat displaced out of this plane.

We can now calculate the z coordinate for the H atom, which is the only coordinate not determined from diffraction data, by assuming that $R = 2.27 \text{ \AA}$, and the values of the x and y coordinate from Table 1. We then obtain two values for the z coordinate, and we reject one of these because it leads to an unreasonable long O-H distance ($z = -0.615$, O-H = 1.35 \AA). We are then left with the H atom in the following position

$$\text{H: } x = 0.013 \quad y = 0.687 \quad z = -0.412.$$

From this position we calculate the following distances and angles:

O(3)-H	0.971 \AA
H---O(2')	1.592 \AA
Angle C-O-H	110.1°

We can also calculate the interpair contribution to the van Vleck second moment from the given H coordinates; we find $M_{2e} = 0.58 \text{ G}^2$, which is in reasonable agreement with the experimental result, $\beta^2 = 0.53 \text{ G}^2$.

The structure of the $(\text{HCO}_3)_2^{2-}$ ion as determined from the neutron diffraction study, and with the z coordinate for the H atom from this study, is shown in Fig. 3. From this Figure it can be seen that the heavy atoms of the $(\text{HCO}_3)_2^{2-}$ ion are coplanar within the experimental uncertainty, but the H atoms are displaced about 0.17 \AA out on each side of the plane. Furthermore, the hydrogen bonds are not linear, but slightly bent. The H atoms are probably forced out of the plane owing to their mutual van der Waals interaction, and the hydrogen bonds deviate from linearity also because of the resistance of opening the H-O-C angle to 120°. These two hindering factors are probably always present in dimers of type (I), not making the dimer structure as stable as the ideal picture (I) indicates. It is therefore understandable that only in potassium bicarbonate is the dimer found, but in other bicarbonates the ions are arranged in chains (Sass & Scheurman, 1964) or bound to water molecules (Bacon & Curry, 1956), where linear hydrogen bonds are easier formed.

The shape of the $(\text{HCO}_3)_2^{2-}$ ion as shown in Fig. 3 indicates that the dimer consists of two fairly loosely bound HCO_3^- ions. Surprisingly enough, the O-H bond does not seem to be significantly stretched under the influence of the relatively short hydrogen bond, 2.54 \AA , as found in other compounds (Hamilton, 1962).

We have not given any error limits on the dimensions found, because the uncertainties of the coordinates in

Table 1 are not directly accessible. The x and y coordinates were obtained through a least-squares refinement to a final reliability index of $R=0.084$ by Herpin & Meriel (1964) indicating that the estimated standard deviation in these coordinates should be about 0.01 \AA . The z coordinate of the H atom is also determined with the same accuracy as outlined above. The uncertainties in the z coordinates of the heavy atoms, however, are probably larger than this as they have been obtained directly from the (001) electron density projection (Herpin, 1952). However, the coordinates in Table 1 seem to give a very consistent picture of the structure of the $(\text{HCO}_3)_2^-$ ion as apparent from inspection of Fig. 1 and Fig. 3, indicating that the given atomic positions are accurate to about 0.01 \AA .

References

- BACON, G. E. & CURRY, N. A. (1956). *Acta Cryst.* **9**, 82.
 HAMILTON, W. C. (1962). *Ann. Rev. Phys. Chem.* **13**, 19.
 HERPIN, P. (1952). *C. r. Acad. Sci. Paris*, **234**, 2205.
 HERPIN, P. & MERIEL, P. (1964). *J. Phys.* **25**, 484.
 KUME, K. & KAKIUCHI, Y. (1960). *J. Phys. Soc. Japan*, **15**, 1277.
 NITTA, I., TOMIIE, Y. & KOO, C. H. (1952). *Acta Cryst.* **5**, 292.
 NITTA, I., TOMIIE, Y. & KOO, C. H. (1954). *Acta Cryst.* **7**, 140.
 PEDERSEN, B. (1968). *Acta Chem. Scand.* To be published.
 PEDERSEN, B. F. & PEDERSEN, B. (1967). *Selected Topics in Structure Chemistry*, p. 253. Oslo Univ. Press.
 ROBERTSON, J. H. (1964). *Acta Cryst.* **17**, 316.
 SASS, R. L. & SCHEUERMAN, R. F. (1962). *Acta Cryst.* **15**, 77.

Acta Cryst. (1968). **B24**, 480

The Crystal Structure of $\text{Pu}_3\text{Zn}_{22}$

BY QUINTIN JOHNSON, DAVID H. WOOD AND GORDON S. SMITH

Lawrence Radiation Laboratory, University of California, Livermore, California, U.S.A.

(Received 29 June 1967)

The structure of a compound present in the Pu–Zn system at the approximate stoichiometry $\text{PuZn}_{7.7}$ has been determined from diffractometrically recorded, single-crystal intensities. The unit cell, containing four formula units of $\text{Pu}_3\text{Zn}_{22}$, is body-centered tetragonal with $a=8.85$, $c=21.18 \text{ \AA}$. The calculated density is 8.71 g.cm^{-3} , and the space group is $I4_1/amd$. This structure also accounts for the published powder pattern of a compound in the Ce–Zn system. Cell constants for $\text{Ce}_3\text{Zn}_{22}$ are $a=8.930$, $c=21.36 \text{ \AA}$.

Introduction

A compound with the approximate composition $\text{PuZn}_{7.7}$ was discovered in a phase-relation study of the zinc-rich region of the Pu–Zn system (Cramer & Wood, 1967). The composition and symmetry indicated this to be a new structure type; we have carried out a determination of this structure to establish the actual composition of this material.

Experimental

Details concerning the preparation of $\text{Pu}_3\text{Zn}_{22}$ are given by Cramer & Wood (1967). To minimize accidental contamination as well as to protect from the atmosphere, crystals were coated with Canada balsam dissolved in xylene. This procedure proved to be more convenient than the use of capillaries, yet provided adequate protection from the radioactive hazards of plutonium.

Single-crystal oscillation, Weissenberg and precession photos showed tetragonal symmetry. The systematic extinctions [$h+k+l \neq 2n$; $hk0: h, (k) \neq 2n$; $hhl: (l \neq 2n)$; $2h+l \neq 4n$] and the $4/mmm$ Laue symmetry uniquely characterize the space group $I4_1/amd$. Lattice

constants, $a=8.85$ and $c=21.18 \text{ \AA}$, were obtained from uncalibrated Weissenberg and precession photographs and are thought to be accurate to about 0.3% .

Intensities were recorded diffractometrically with use of zirconium filtered Mo $K\alpha$ radiation ($\lambda=0.7107 \text{ \AA}$). A total of 229 independent reflections were measured up to a 2θ value of 40° . The shape of the crystal resembled a distorted cylinder. A 2θ -dependent absorption correction was applied assuming a cylindrical shape ($\mu r=3.0$). In addition, a pronounced dependence of intensity with respect to φ was observed. An attempt to remove this dependency was made by measuring the intensities of several reflections at $\chi=90^\circ$ as a function of φ and applying the indicated correction to all data dependent only on the φ value at which the reflection was observed. This correction, which amounted to $\pm 50\%$, was modified in the course of refinements as will be discussed later.

Determination of the structure

Precession photos of $\text{Pu}_3\text{Zn}_{22}$ were quite similar to those of the $\text{Th}_2\text{Ni}_{17}$ - and $\text{Th}_2\text{Zn}_{17}$ -like compounds of Pu–Zn. For example, the $hk0$ zone of $\text{Pu}_3\text{Zn}_{22}$ could be mistaken for the hhl zone of $\text{Pu}_2\text{Zn}_{17}$ ($\text{Th}_2\text{Ni}_{17}$ -like).