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NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C. 20234

The Crystal Structures of $CaNa_2(CO_3)_2 \cdot 5H_2O$, Synthetic Gaylussite, and $CaNa_2(CO_3)_2 \cdot 2H_2O$, Synthetic Pirssonite

BY BRIAN DICKENS AND WALTER E. BROWN[1]

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The crystal structure of $CaNa_2(CO_3)_2 \cdot 5H_2O$ (synthetic gaylussite) has been determined from 2988 single-crystal X-ray diffraction data collected by a counter method. The unit cell parameters are $a = 14.361 \pm 0.002$ Å, $b = 7.781 \pm 0.001$ Å, $c = 11.209 \pm 0.002$ Å, and $\beta = 127.84 \pm 0.01°$, and the space group is C2/c. There are four formula weights per cell. The calculated density is 1.99 g/ml; the observed density is also 1.99 g/ml. $R_w = (\Sigma(w||F_o| - |F_c||)^2/\Sigma(w|F_o|)^2)^{1/2} = 0.043$; $R = 0.054$. The hydrogen atoms have been located approximately. Two CO_3 anions, at a dihedral angle of 134.3° to one another, are ionically bonded edgewise to a Ca ion to form a $Ca(CO_3)_2$ triplet. The bonded edges of the CO_3 groups are very nearly parallel. Both CO_3 groups in a triplet are further bonded to a pair of Na ions which are also bonded to adjacent triplets. Four of the water molecules are bonded to Ca and form hydrogen bonds to CO_3 groups in neighboring triplets. The fifth water molecule is bonded to two Na ions and is hydrogen bonded to two water molecules. One hydrogen appears to be only 2.2–2.5 Å from the Na. The crystal structure of $CaNa_2(CO_3)_2 \cdot 2H_2O$ (synthetic pirssonite) has also been determined from 1141 single-crystal X-ray diffraction data collected by a counter method. The unit cell parameters are $a = 11.340 \pm 0.004$ Å, $b = 20.096 \pm 0.005$ Å, and $c = 6.034 \pm 0.002$ Å, and the space group is Fdd2. There are eight formula weights per cell. The calculated density is 2.35 g/ml; the observed density is also 2.35 g/ml; $R_w = 0.029$; $R = 0.044$. The hydrogen atoms have been located approximately. As in $CaNa_2(CO_3)_2 \cdot 5H_2O$, two CO_3 anions are bonded edgewise to a Ca ion to form a triplet. In this triplet, the Ca, the two carbons, and the CO_3 oxygens remote from Ca lie nearly on a line, but the CO_3 groups have twisted about this axis so that the bonded edges are nearly at right angles to one another; the dihedral angle is 95.5°. In contrast to $CaNa_2(CO_3)_2 \cdot 5H_2O$, each CO_3 anion is also bonded to a second Ca ion to form a three-dimensional network. The Na ions and water molecules form an alternating chain along $[01\bar{1}]$. Each Na ion is coordinated to four oxygens in CO_3 anions and to two water molecules. The water molecules are primarily coordinated to Ca ions and form hydrogen bonds with neighboring CO_3 anions. The $H_2O \cdots Na$ bonding is thought to be weak.

Introduction

The two hydrated calcium sodium carbonate minerals gaylussite,[2a] $CaNa_2(CO_3)_2 \cdot 5H_2O$, and pirssonite,[2b] $CaNa_2(CO_3)_2 \cdot 2H_2O$, have been known since 1826 and 1896, respectively. They occur as deposits from soda lakes which are commercial sources of trona, $Na_3H(CO_3)_2 \cdot 2H_2O$, are stable phases in the system Na_2CO_3–$CaCO_3$–H_2O, and are likely to occur under evaporative conditions such as in turbines and heating systems when these components are present. Interest in these salts also stems from the importance of calcium carbonates in biological mineralization. Although $CaNa_2(CO_3)_2 \cdot 5H_2O$ and $CaNa_2(CO_3)_2 \cdot 2H_2O$ are not known to participate in biological mineralization, a knowledge of their structures provides basic information about the interactions between calcium and carbonate ions and the hydration of calcium ions. The crystal structures of synthetic $CaNa_2(CO_3)_2 \cdot 5H_2O$ and synthetic $CaNa_2(CO_3)_2 \cdot 2H_2O$ have been determined by single-crystal X-ray diffraction studies and are reported here. Work on both of these structures was completed before that of Corazza and Sabelli[3] on pirssonite came to our attention.

Determination of the Structure of $CaNa_2(CO_3)_2 \cdot 5H_2O$

Crystals of $CaNa_2(CO_3)_2 \cdot 5H_2O$ were grown in beakers containing 100 ml of water, 18 g of Na_2CO_3, 10 g of $CaCl_2$, and 800 ppm of sodium polyphosphate, combining the procedures of Bury and Redd[4] and Brooks, Clark, and Thurston.[5] The initial solid phase was mostly spherulites, probably of $CaCO_3 \cdot H_2O$. On standing, these dissolved and good single crystals of $CaNa_2(CO_3)_2 \cdot 5H_2O$ were formed.

A single crystal of $CaNa_2(CO_3)_2 \cdot 5H_2O$, maximum dimension about 0.3 mm, minimum dimension about 0.2 mm ($\mu_{MoK\alpha} = 8$ cm^{-1}), was sealed in a borate glass capillary to prevent dehydration. The cell dimensions at 24° were refined from 25 2θ values obtained with a diffractometer[6] to yield $a = 14.361 \pm 0.002$ Å, $b = 7.781 \pm 0.001$ Å, $c = 11.209 \pm 0.002$ Å, and $\beta = 127.84 \pm 0.01°$, assuming λ(Mo Kα) 0.71069 Å, for the cell with space group C2/c or Cc (reciprocal lattice extinctions observed on precession films to be $h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$). The uncertainties quoted on cell dimensions are standard errors computed from least-squares refinements of the cell dimensions to fit observed 2θ values. The most obvious cell is body centered, with axial ratios which correspond to those given by Dana.[2a] The space groups C2/c and Cc were chosen using crystallographic convention.[7] The calculated density with $z = 4$ is 1.99 g/ml; the observed density[2a] is also 1.99 g/ml.

The intensities of reflections with 2θ values up to 80° in a hemisphere of the reciprocal lattice were measured

(1) Director, Research Associate Program of the American Dental Association at the National Bureau of Standards.

(2) C. Palache, H. Berman, and C. Frondel, "Dana's System of Mineralogy," Vol. II, 7th ed, John Wiley & Sons, Inc., New York, N. Y., 1951: (a) p 234; (b) p 232.

(3) E. Corazza and C. Sabelli, *Acta Cryst.*, **23**, 763 (1967).

(4) C. R. Bury and R. Redd, *J. Chem. Soc.*, 1160 (1933).

(5) R. Brooks, L. M. Clark, and E. F. Thurston, *Phil. Trans. Roy. Soc. London*, **A243**, 145 (1951).

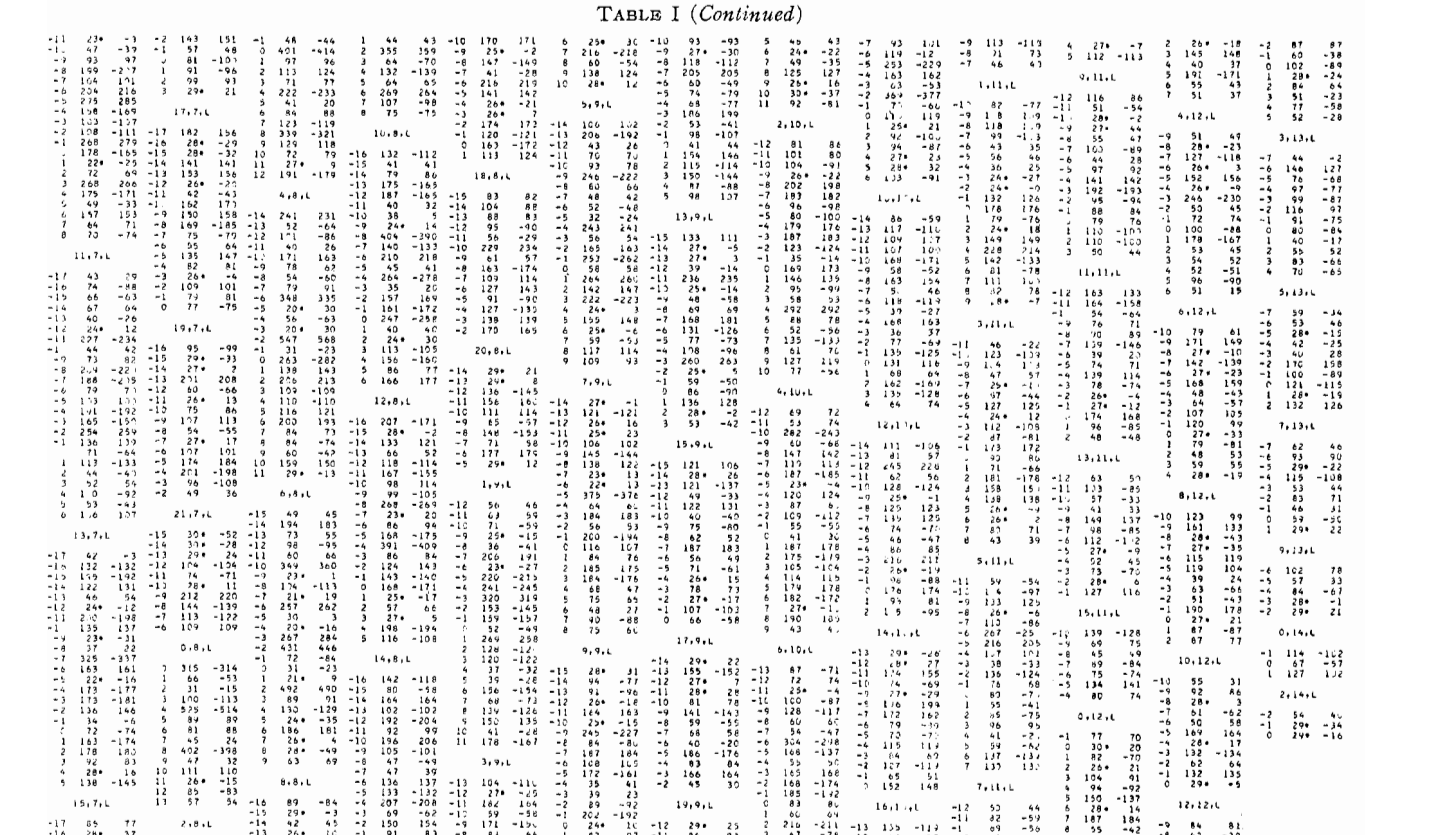
(6) F. A. Mauer and A. L. Koenig, Summer Meeting of the American Crystallographic Association, University of Minnesota, Minneapolis, Minn., Aug 1967, Paper 10.

(7) "International Tables for Crystallography," The Kynoch Press, Brimingham, England, 1962.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $CaNa_2(CO_3)_2 \cdot 5H_2O$[a]

TABLE I (*Continued*)



[a] Columns are l, $10F_o$, and $10F_c$; F_o and F_c are on an absolute scale. Reflections marked with an asterisk are "unobserved."

on a diffractometer[6] using Mo Kα radiation with a 4° takeoff angle, a 0.001-in. Nb filter, and the peak-height method.[8] The peak-to-intensity curve was established from 48 suitable reflections, spread uniformly over the 2θ range, which were measured by peak heights and by scanning. The data were merged into 2988 unique reflections, of which 2632 were of observable intensity. Since serious errors in peak height measurements are usually caused by measuring the background too near an adjacent peak, by slight misalignment of the crystal, or by absorption, in all of which cases the observed F_{hkl} would be too small, any supposedly equivalent values of F_{hkl} which were not within 10% of one another were not averaged. Instead, the larger of the two was taken as the observed F_{hkl}. The discrepancy value, $\Sigma||F_t| - |F_t'||/|\Sigma F_t|$, between reflections accepted as equivalent was 0.045, based on F's. (Although the anisotropy of the mosaic spread of the crystal also affects the peak heights, in this case the peak height method provided data of sufficient accuracy.) The maximum error caused by the fact that no corrections for absorption were made is about 6% of an observed intensity. The intensity, I, of a reflection was taken as $P - (T/2T_B)(B_L + B_H)$ with standard deviation $\sigma(I) = (P + (B_L + B_H)(T/(2T_B))^2)^{1/2}$. The structure factor is then $((AF)(Lp)I)^{1/2}$ with standard deviation $\sigma(F) = (\sigma(I)/2)(Lp/I)^{1/2}$. P is the counts at the peak (corrected from peak heights to θ–2θ scans), B_L and B_H are the background counts at lower and higher 2θ, respectively; T is the time spent counting the peak; T_B is the time spent counting the background; AF is the attenuator factor; and Lp is the Lorentz–polarization factor. Any intensity which was more than 2σ above background was considered to be observed. The Lp factor used is $2 \sin 2\theta/(1 + \cos^2 2\theta)$.

The subsequent calculations were all performed using the crystallographic computing system (X-ray 63) assembled under the editorship of J. M. Stewart at the University of Maryland. The quasinormalized structure factors[9] ($\langle|E^2|\rangle$ made equal to 1) were calculated. The statistics are $\langle|E|\rangle = 0.816$ ($C = 0.798$ and $A = 0.886$), $\langle|E^2 - 1|\rangle = 0.922$ ($C = 0.968$ and $A = 0.736$), % of E's $> 3.0 = 0.09$ ($C = 0.3$ and $A = 0.01$), % of E's $> 2.0 = 3.7$ ($C = 4.6$ and $A = 1.8$), and % of E's $> 1.0 = 34.1$ ($C = 31.7$ and $A = 36.8$), where C and A are the theoretical values for centric and acentric structures, respectively. These sta-

(8) See C. W. Reimann, A. D. Mighell, and F. A. Mauer, *Acta Cryst.*, **23**, 135 (1967), for a detailed description of the method of data collection.

(9) See C. Dickinson, J. M. Stewart, and J. R. Holden, *ibid.*, **21**, 663 (1966), for the method used in estimating the quasinormalized structure factors.

TABLE II

ATOMIC PARAMETERS OF $CaNa_2(CO_3)_2 \cdot 5H_2O$[a]

Atoms	x	y	z	B_{11}[b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca	0.0000	0.1929 (1)	0.2500	0.59 (1)	1.27 (2)	0.86 (2)		0.41 (1)	
Na	0.0881 (1)	0.1822 (1)	−0.0107 (1)	1.56 (3)	1.92 (3)	1.67 (3)	0.06 (3)	1.12 (3)	−0.16 (3)
C	0.1853 (2)	−0.0286 (2)	0.3161 (2)	0.94 (6)	1.18 (6)	1.18 (6)	0.01 (5)	0.65 (5)	0.11 (5)
O(1)	0.2852 (1)	−0.0906 (2)	0.3633 (2)	1.26 (5)	2.88 (6)	1.85 (6)	0.96 (4)	1.13 (5)	0.67 (5)
O(2)	0.1033 (1)	0.0031 (2)	0.1749 (1)	1.07 (4)	2.09 (5)	0.90 (5)	0.01 (4)	0.44 (4)	−0.01 (4)
O(3)	0.1658 (1)	0.0095 (2)	0.4113 (1)	0.94 (4)	1.97 (5)	0.99 (5)	0.10 (4)	0.67 (4)	0.00 (4)
O(4)	0.0000	0.6791 (3)	0.2500	1.84 (8)	1.90 (8)	2.22 (9)		1.16 (8)	
O(5)	0.0696 (1)	0.2935 (2)	0.5029 (2)	1.44 (5)	2.02 (6)	1.50 (5)	0.13 (5)	0.83 (5)	−0.06 (5)
O(6)	0.1467 (1)	0.4048 (2)	0.3109 (2)	1.12 (5)	2.60 (5)	1.27 (5)	−0.47 (5)	0.76 (4)	−0.22 (5)

[a] Figures in parentheses are computed standard errors in last significant figures quoted and were obtained in the full-matrix least-squares refinements. Average shift per error for the last cycle is 0.23. [b] Units of thermal parameters are Å². The form of the thermal ellipsoid is $\exp[-1/4(a^{*2}B_{11}h^2 + b^{*2}B_{22}k^2 + c^{*2}B_{33}l^2 + 2a^*b^*B_{12}hk + 2a^*c^*B_{13}hl + 2b^*c^*B_{23}kl)]$.

TABLE III

THE HYDROGEN POSITIONS IN $CaNa_2(CO_3)_2 \cdot 5H_2O$

	Electron density difference map			Least-squares refinement[a]			Calcd[b]		
	x	y	z	x	y	z	x	y	z
H(1)	0.05	0.60	0.27	0.05	0.60	0.27	0.06	0.60	0.28
H(1)	0.11	0.22	0.57	0.10	0.21	0.55	0.09	0.20	0.57
H(3)	0.10	0.37	0.54	0.11	0.38	0.54	0.12	0.38	0.56
H(4)	0.20	0.43	0.39	0.20	0.44	0.40	0.21	0.44	0.41
H(5)	0.17	0.40	0.27	0.16	0.39	0.27	0.17	0.41	0.25

[a] The computed standard random errors are 0.002 in the x coordinates and 0.003 in the y and z coordinates. In the authors' opinion, the systematic errors known to accompany the location of covalently bonded hydrogen atoms by X-ray methods are about an order of magnitude larger than this. [b] Calculated with imposed H_2O geometry (see text). These positions were used in the calculation of the interatomic distances.

tistics indicate that the space group is centrosymmetric, C2/c, instead of noncentrosymmetric, Cc. This choice was subsequently verified by the structure determination. The atomic scattering factors used were taken from ref 10, except for those of hydrogen, which were taken from ref 11. The quantity $\Sigma(w||F_o| - |F_c||)^2$ was minimized in the full-matrix least-squares refinements. The least-squares weight for each reflection was taken as $1/(\sigma(F))^2$, normalized so that the maximum weight was 1. The least-squares refinements included with full weights unobserved reflections which calculated greater than 2σ above background.

The structure was solved from the sharpened Patterson function, calculated from the $(E^2 - 1)$ coefficients and from subsequent F_o Fourier syntheses. It was refined isotropically to $R_w = 0.079$ allowing the scale factor, the positional parameters, and the thermal parameters to vary. The structure was then refined anisotropically to $R_w = 0.061$. The hydrogens were located from a difference synthesis in which the coefficients were weighted as in the least-squares refinements. One spurious peak, about 0.8 Å from Ca, was as high as the hydrogen peaks; otherwise the hydrogen locations were unambiguous. The next largest peak was about half the height of the hydrogen peaks. Inclusion of these hydrogens with fixed thermal parameters ($B_H = 1.0$ Å²) in the refinements decreased R_w to 0.043 and R to 0.054. In these refinements 87 of the 356 unobserved reflections were included with full weights: the rest were given zero weights. The observed and calculated structure factors are given in Table I. The parameters for atoms other than hydrogen are given in Table II. The hydrogen positions derived from the electron density map and the refined positions are given in Table III along with positions calculated with the geometry of the free water molecule imposed. The interatomic distances quoted in the text are based on these calculated positions of the hydrogens.

The largest correlation coefficients are 0.25 between the scale factor and the Ca B_{11} anisotropic temperature factor, 0.75 between the Ca B_{33} and B_{13} anisotropic temperature factors, 0.68 between the Na x and z parameters, and 0.78 between the Na B_{33} and B_{13} thermal parameters. Most coefficients are, however, much less than 0.04.

Discussion of the Structure of $CaNa_2(CO_3)_2 \cdot 5H_2O$

General Features.—The structure (Figure 1) contains $Ca(CO_3)_2$ triplets in which the Ca, lying on a diad, bonds to edges of the two CO_3 groups. The two edges are very nearly parallel, and the planes of the CO_3 groups form a dihedral angle of 134.3°. Two Na ions in the reentrant dihedral angle are each bonded to both CO_3 groups. These Na ions are each bonded to two water molecules and to an oxygen of a CO_3 group in each of two neighboring triplets, thus providing three-dimensional bonding. The two sets of water molecules in general positions O(5) and O(6) are bonded to the Ca and are hydrogen bonded to CO_3 oxygens to provide additional three-dimensional bonding. The only hydrogen bonding between water molecules appears to be provided by O(4) which is the only water not bonded to Ca.

(10) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202.

(11) R. McWeeny, *Acta Cryst.*, **4**, 513 (1951).

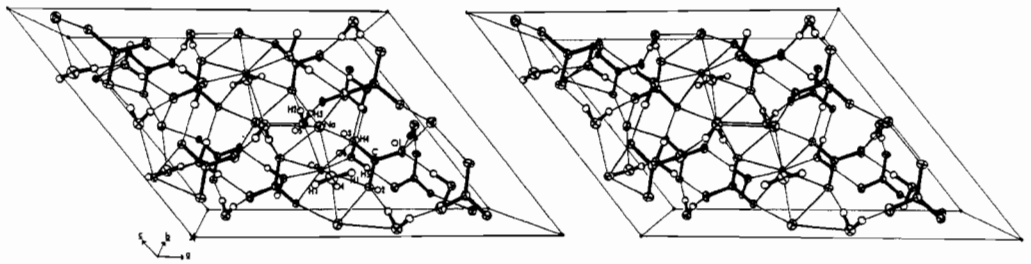


Figure 1.—Stereoscopic view along [010] of unit cell of $CaNa_2(CO_3)_2 \cdot 5H_2O$. The star indicates the origin of the coordinate system.

The Calcium Environment.—The immediate Ca environment is summarized in Table IV and in Figure 2. Both CO_3 groups are coordinated (*via* O(2) and O(3)) to Ca; the coordination of Ca is completed by four water molecules, O(5), O(5′), O(6), and O(6′). These Ca···O distances are within the normal range. The strongest possible ionic repulsion in the structure, the Ca···Ca interaction, is minimized by the Ca ions being widely separated from one another (Ca···Ca > 4.5 Å).

TABLE IV

THE CALCIUM ENVIRONMENT IN $CaNa_2(CO_3)_2 \cdot 5H_2O$

Atoms	Distance, Å	Atoms	Distance, Å
Ca–O(2)	2.573 (2)[a]	Ca–O(6)	2.420 (2)
Ca–O(3)	2.385 (1)	Ca–O(4)	3.783 (2)
Ca–O(5)	2.484 (2)	Ca–O(4″)	3.997 (2)

[a] In all distances and angles quoted in this paper the values in parentheses are the computed standard errors in the last significant figures.

The Carbonate Group.—The CO_3 group is essentially planar with an average C–O distance of 1.288 Å. Its dimensions and environment are summarized in Table V and Figure 3. Oxygen O(1) is bonded to Na (2.314 Å) and is hydrogen bonded to water oxygens O(5) (2.847 Å) *via* H(3) (~1.9 Å) and O(6) (2.667 Å) *via* H(5) (~1.7 Å). Oxygen O(2) is bonded to Ca (2.573 Å), Na (2.400 Å), and Na′ (2.610 Å), and is hydrogen bonded to O(5) (2.852 Å) *via* H(2) (~1.9 Å). Oxygen O(3) is bonded to Ca (2.385 Å) and Na (2.331 Å) and is hydrogen bonded to O(6) (2.666 Å) *via* H(4) (~1.7 Å). The observed C–O bond distances correlate qualitatively with the oxygen environments. Oxygens O(2) and O(3), which are the ones bonded to the Ca, have longer bond distances to the carbon than does O(1). Similarly, the O(2)–C–O(3) bond angle, 118.1°, is less than 120°, apparently because coordination to Ca pulls these oxygens together.

The two CO_3 groups in a triplet are also coordinated to two Na ions (Figure 2) each of which can bond to both CO_3 groups since the dihedral angle between the planes of the two CO_3 groups is 134.3°. This coordination is instrumental in making the O(2)–O(3) vector in one CO_3 group very nearly parallel to the O(2′)–O(3′) vector in the other CO_3 group. The Ca ion is 0.69 Å below the intersection of the planes of these CO_3 groups.

Every CO_3 ion is inclined to (010) by 23°, making *b* the axis most nearly parallel to the direction in these ions which contributes the least to the index of refraction. This is an agreement with the observation that *b* is the direction of lowest index of refraction.

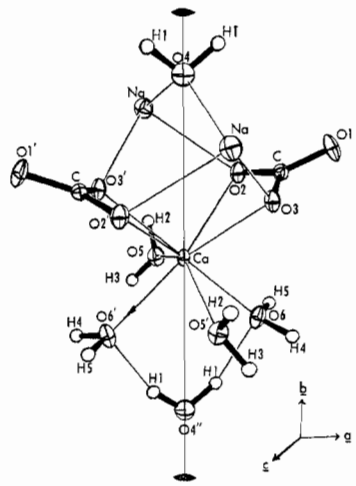


Figure 2.—The calcium ion environment in $CaNa_2(CO_3)_2 \cdot 5H_2O$. Primed atoms are related to unprimed atoms by the twofold axis.

TABLE V

THE CARBONATE ANION AND ITS ENVIRONMENT IN $CaNa_2(CO_3)_2 \cdot 5H_2O$

Atoms	Distance, Å
C–O(1)	1.280 (3)
C–O(2)	1.291 (2)
C–O(3)	1.293 (3)
O(1)–O(2)	2.247 (2)
O(1)–O(3)	2.229 (3)
O(2)–O(3)	2.216 (2)

Coordinated atoms	Angle, deg
O(1)–C–O(2)	121.8 (2)
O(1)–C–O(3)	120.1 (2)
O(2)–C–O(3)	118.1 (2)

O(1) environment	
Atoms	Distance, Å
O(1)–O(5)	2.847 (2)
O(1)–H(3)	1.91[a]
O(1)–Na	2.341 (2)
O(1)–O(6)	2.667 (3)
O(1)–H(5)	1.71[a]

O(2) environment	
Atoms	Distance, Å
O(2)–Ca	2.573 (2)
O(2)–Na	2.400 (2)
O(2)–Na′	2.610 (2)
O(2)–O(5)	2.852 (2)
O(2)–O(6)	3.364 (2)
O(2)–O(4)	3.285 (2)
O(2)–H(2)	1.91[a]

O(3) environment	
Atoms	Distance, Å
O(3)–Ca	2.385 (1)
O(3)–O(5)	3.096 (3)
O(3)–O(4)	3.204 (2)
O(3)–Na	2.331 (2)
O(3)–O(6)	2.666 (2)
O(3)–H(4)	1.71[a]

[a] The O···H distances were derived from the hydrogen positions, calculated with imposed water geometry, given in Table III.

The Na Environment.—The Na is coordinated (Table VI and Figure 4) approximately octahedrally by O(1), O(2), O(2′), and O(3′), all in different CO_3 groups, and

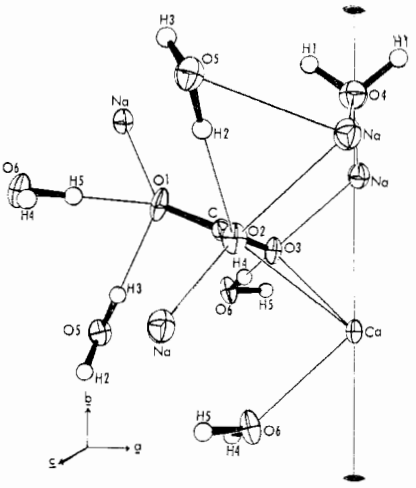


Figure 3.—The carbonate anion environment in $CaNa_2(CO_3)_2 \cdot 5H_2O$.

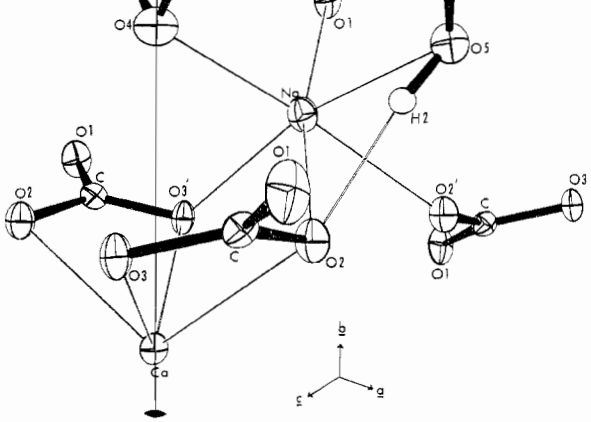


Figure 4.—The sodium ion environment in $CaNa_2(CO_3)_2 \cdot 5H_2O$.

the O(4) and O(5) waters. The Ca···Na closest approach is 3.626 Å across O(2) and O(3′) (Figure 2) of the two CO_3 groups bonded to the Ca.

TABLE VI

THE SODIUM ENVIRONMENT IN $CaNa_2(CO_3)_2 \cdot 5H_2O$

Atoms	Distance, Å	Atoms	Distance, Å
Na–O(2′)	2.400 (2)	Na–O(4)	2.408 (1)
Na–O(2)	2.610 (2)	Na–O(5)	2.475 (2)
Na–O(3′)	2.331 (2)	Na–O(1)	2.341 (2)

The Water Environments and the Hydrogen Positions.—The hydrogen positions (Table III) appeared to be unambiguous in the difference electron density synthesis. The least-squares refinement shifted these positions an average of 0.11 Å. The average O–H distance for both of the above sets, 0.79 Å, reflects the well-known asymmetry of the electron distribution around a covalently bonded hydrogen. More realistic hydrogen positions were calculated assuming (a) free water geometry with an O–H length of 0.956 Å and an H–O–H bond angle of 104.5° and (b) maximum linearity of the O–H···O bonds. The values for the bond angles obtained in this way ranged from 161 to 178°, *i.e.*, the normal range.

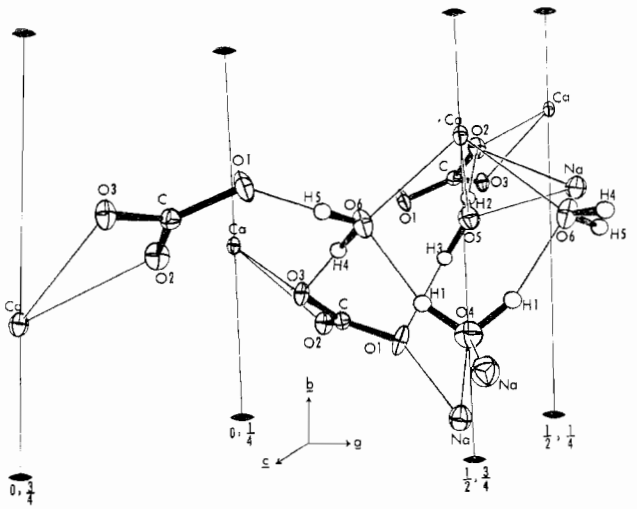


Figure 5.—The water environments and hydrogen bonding in $CaNa_2(CO_3)_2 \cdot 5H_2O$.

With one possible exception, this method produced a reasonable hydrogen-bonding scheme as follows (Table VII and Figure 5). O(4), which lies on the diad, is the donor in the bond to O(6) (2.774 Å) *via* H(1) in the only hydrogen bonding between water molecules. O(5) is the donor in the bonds to O(2) (2.852 Å), *via* H(2), and in the bond to O(1) (2.847 Å), *via* H(3). O(2) and O(1) are in CO_3 groups in separate triplets. O(6) is the donor in the bond to O(3) (2.666 Å) *via* H(4) and in the bond to O(1) (2.667 Å) of another triplet *via* H(5). This creates a three-dimensional hydrogen-

TABLE VII

THE WATER ENVIRONMENTS IN $CaNa_2(CO_3)_2 \cdot 5H_2O$

(1) The Environment of Water H(1)–O(4)–H(1′)

Atoms	Distance, Å	Coordinated atoms	Angle, deg
O(4)–O(6)	2.774 (2)	O(6)–O(4)–O(6′)	79.37 (8)
O(4)–Na	2.408 (1)	O(4)–H(1)–O(6)	161
H(1)–O(6)	1.85		

(2) The Environment of Water H(2)–O(5)–H(3)

Atoms	Distance, Å	Coordinated atoms	Angle, deg
O(5)–Ca	2.484 (2)	O(1)–O(5)–O(2)	122.36 (6)
O(5)–O(1)	2.847 (2)	O(5)–H(2)–O(2)	167
O(5)–O(2)	2.852 (2)	O(5)–H(3)–O(1)	167
O(5)–Na	2.475 (2)		
H(2)–O(2)	1.91		
H(3)–O(1)	1.91		
H(2)–Na	2.21		
H(2)–Ca	3.01		

(3) The Environment of Water H(4)–O(6)–H(5)

Atoms	Distance, Å	Coordinated atoms	Angle, deg
O(6)–Ca	2.420 (2)	O(1)–O(6)–O(3)	106.87 (8)
O(6)–O(4)	2.774 (2)	O(6)–H(4)–O(3)	178
O(6)–H(1)	1.85	O(6)–H(5)–O(1)	178
O(6)–O(3)	2.666 (3)		
O(6)–O(1)	2.667 (3)		
H(4)–O(3)	1.71		
H(5)–O(1)	1.71		

bonding network with H···O distances in the reasonable range 1.71–1.91 Å. The five shortest interoxygen distances, exclusive of those within the CO_3 groups, correspond to hydrogen bonds. This scheme results in the relatively short H(2)–Na distance of 2.21 Å. However, relocating H(2) or H(3) to any of the four next nearest oxygen neighbors, O(2) (3.208 Å), O(6) (3.060 Å), O(6′) (3.087 Å), or O(3) (3.096 Å), would put it into an edge of the Ca coordination. Locating H(2) and H(3) on the side of O(5) away from Ca and Na, as in the present scheme, places them in suitable positions to form hydrogen bonds to the two oxygen neighbors nearest O(5). This position approximately equalizes the electrostatic forces repelling H(2) from Na and Ca. Thus, although H(2) is in the edge of the Na coordination, it presumably is repelled less there than in other possible positions. Furthermore, there is no indication in the difference map that H(2) or H(3) should be placed differently.

Thermal Parameters.—The Ca has its largest component of thermal motion parallel to b, which corresponds to the direction of apparent least constraint. The ellipsoids of Na, C, and O(4) are nearly spherical. The major motion of the CO_3 group appears to be a rocking about C with the principal component of each oxygen being roughly parallel to b. Water molecule oxygens O(5) and O(6) have their largest components normal to the Ca···O bonds.

Determination of the Crystal Structure of $CaNa_2(CO_3)_2\cdot 2H_2O$

We determined the crystal structure of $CaNa_2(CO_3)_2\cdot 2H_2O$, the synthetic counterpart of the mineral pirssonite, before the recent work of Corazza and Sabelli[3] came to our attention. There are enough differences in the two procedures to warrant a brief description of our determination. They used a mineral specimen ground to a sphere of 0.616-mm diameter, measured 481 reflections of observable intensity from integrated films with a microdensitometer, corrected for absorption, and refined using block-diagonal least squares to $R = 0.057$ using isotropic temperature factors.

In the present work, good crystals of synthetic $CaNa_2(CO_3)_2\cdot 2H_2O$ were grown at 50° from a water solution of 27% Na_2CO_3 and 5% NaOH by weight, in contact with a powder of the calcite phase of synthetic $CaCO_3$.[4] A small crystal, maximum dimension about 0.20 mm, minimum dimension about 0.05 mm ($\mu_{Mo} = 10.3$ cm^{-1}), of $CaNa_2(CO_3)_2\cdot 2H_2O$ was selected. The cell dimensions were determined at 24°, assuming λ(Mo Kα) 0.71069 Å, to be $a = 11.340 \pm 0.004$, $b = 20.096 \pm 0.005$, and $c = 6.034 \pm 0.002$ Å from 2θ values of axial reflections observed on a diffractometer. [The uncertainties quoted on cell dimensions are estimates based on experience with the technique and in the authors' opinion may be treated as standard errors.] Evans[12] reported the dimensions $a = 11.32 \pm 0.02$, $b = 20.02 \pm 0.02$, and $c = 6.00 \pm 0.02$ Å, with $z = 8$, and that the space group is Fdd2. Over 2200 reflections from two octants of the reciprocal lattice were measured on a diffractometer[6] with the peak height procedure used for $CaNa_2(CO_3)_2\cdot 5H_2O$. These data were merged into a unique set of 1141 reflections, 1079 of which were of observable intensity. The R value between reflections accepted as equivalent was 0.027 based on F's. The quasinormalized structure factor statistics confirm the acentricity of the space group. Weights calculated as for $CaNa_2(CO_3)_2\cdot 5H_2O$ were used in the full-matrix least-squares refinements. The atomic scattering factors used for $CaNa_2(CO_3)_2\cdot 5H_2O$ were also used for $CaNa_2(CO_3)_2\cdot 2H_2O$. No corrections for absorption were made, causing a maximum error of about 12% in an observed intensity.

All atoms other than the water molecule were found from the sharpened Patterson map. The oxygen of the water molecule was found from an F_o Fourier synthesis. The structure was refined isotropically to $R_w = 0.059$ and then anisotropically to $R_w = 0.042$. Twenty-one of the 67 "unobserved" reflections were included in these refinements with full weights. The hydrogen peaks appeared to be unambiguous in the electron density difference synthesis with heights 50% greater than the next highest peak. It was later found that these peaks correspond with the hydrogen positions suggested by Corazza and Sabelli.[3] The hydrogens were included with fixed thermal parameters ($B_H = 1.0$ Å^2), and the structure was refined anisotropically to $R_w = 0.029$ and $R = 0.044$. The largest correlation coefficients are about 0.2 and are between the scale factor and some of the anisotropic temperature factors, between some of the anisotropic temperature factors themselves, and between the x and y parameters of most atoms. Most of the remaining coefficients are less than 0.05. The observed and calculated structure factors are given in Table VIII.

The atomic parameters for atoms other than hydrogen, as obtained by us, and those obtained by Corazza and Sabelli,[3] are given in Table IX. The agreement between the two sets of parameters is excellent. All positional parameters for atoms other than hydrogens are within 2σ when our estimated standard errors are used; four of the eighteen parameters differ by more than 2σ when the estimates of Corazza and Sabelli[3] are used. Their estimates of errors, which are about 60% as large as ours, were derived from the block-diagonal least-squares approximation using only 481 observed reflections and are probably too small. The hydrogen positions obtained from the electron density difference synthesis, from the least-squares refinements, and from a water geometry, imposed as described for $CaNa_2(CO_3)_2\cdot 5H_2O$, are compared in Table X with the ones reported by Corazza and Sabelli. The placement of the hydrogen atoms in our work is recognized as being only approximate. The computed standard errors for the positional parameters of $CaNa_2(CO_3)_2\cdot 2H_2O$ are about four times as great as those of $CaNa_2(CO_3)_2\cdot 5H_2O$. This probably arises from the acentric symmetry of $CaNa_2(CO_3)_2\cdot 2H_2O$ and from its lower ratio of reflections to parameters.

(12) H. T. Evans, *Am. Mineralogist*, **33**, 261 (1948).

TABLE VIII

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $CaNa_2(CO_3)_2 \cdot 2H_2O$[a]

0,K,0		
4	286	291
8	803	833
12	38	38
16	323	322
20	248	262
24	122	126
28	68	64
32	64	66
36	139	109
0,K,2		
2	240	234
6	170	167
10	394	396
14	108	105
18	100	112
22	118	127
26	132	141
30	150	145
34	54	52
0,K,4		
0	387	392
4	197	197
8	208	210
12	140	136
16	222	230
20	149	151
24	74	68
28	97	91
32	33	24
0,K,6		
2	167	177
6	141	146
10	293	306
14	100	105
18	114	116
22	123	122
26	106	106
30	128	119
0,K,8		
0	308	324
4	107	104
8	165	174
12	22	13
16	107	113
20	97	95
24	59	67
0,K,10		
2	74	79
6	120	119
10	88	87
14	99	92
1,K,1		
1	230	218
3	110	107
5	247	246
7	289	285
9	273	264
11	171	174
13	54	60
15	295	301
17	37	30
19	58	60
21	132	135
23	134	137
25	51	54
27	55	58
29	87	76
31	88	90
33	25	24
35	92	81
1,K,3		
1	81	85
3	286	281
5	564	595
7	220	227
9	75	75
11	102	109
13	304	304
15	272	282
17	116	116
19	87	92
21	158	157
23	108	107
25	74	74
27	53	47
29	88	82
31	105	100
33	14*	13
1,K,5		
1	33	32
3	54	58
5	259	268
7	112	118
9	58	59
11	55	61
13	188	192
15	144	148
17	108	112
19	35	32
21	123	122
23	80	75
25	76	81
27	32	27
29	81	76
31	104	94
1,K,7		
1	131	139
3	72	73
5	98	102
7	55	67
9	88	92
11	58	69
13	77	78
15	106	110
17	61	61
19	82	79
21	101	100
23	38	39
25	55	62
27	16*	16
1,K,9		
1	49	57
3	72	69
5	105	108
7	81	83
9	81	84
11	47	50
13	67	72
15	111	109
17	55	49
19	15*	5
2,K,0		
2	290	295
4	71	72
6	100	109
8	440	444
10	385	400
12	218	220
14	30	31
16	41	10
18	239	252
20	75	89
22	44	47
24	28	37
26	141	152
28	72	67
30	70	71
32	35	28
34	99	90
36	16*	12
2,K,2		
0	677	685
2	496	500
4	177	166
6	101	111
8	446	444
10	198	206
12	126	127
14	174	169
16	207	206
18	97	100
20	144	144
22	63	75
24	100	102
26	35	35
28	109	107
30	56	50
32	66	61
34	56	45
2,K,4		
2	190	198
4	164	167
6	167	172
8	42	44
10	187	192
12	43	51
14	149	151
16	48	52
18	97	103
20	39	40
22	142	138
24	72	70
26	61	52
28	30	29
30	125	117
32	53	49
2,K,6		
0	290	290
2	209	218
4	110	115
6	87	90
8	214	223
10	64	60
12	81	85
14	116	121
16	135	139
18	35	36
20	97	98
22	35	29
24	81	81
26	14*	20
28	85	83
30	15*	15
2,K,8		
2	118	123
4	10*	6
6	87	88
8	62	58
10	146	149
12	72	74
14	59	60
16	43	41
18	116	122
20	24	21
22	54	48
24	24	19
2,K,10		
0	108	122
2	68	66
4	47	50
6	29	28
8	92	102
10	36	35
12	58	59
14	69	65
3,K,1		
1	316	304
3	307	305
5	400	399
7	471	469
9	144	144
11	72	69
13	293	291
15	197	193
17	207	212
19	157	164
21	67	69
23	95	92
25	119	118
27	102	96
29	68	88
31	48	45
33	91	84
35	58	43
3,K,3		
1	160	158
3	325	326
5	75	74
7	245	243
9	89	88
11	103	104
13	219	225
15	66	58
17	82	87
19	65	67
21	123	128
23	126	126
25	11*	11
27	31	34
29	88	87
31	77	72
33	71	65
3,K,5		
1	101	103
3	307	317
5	194	199
7	131	134
9	102	101
11	136	137
13	148	151
15	100	102
17	135	133
19	92	89
21	103	98
23	129	124
25	46	46
27	55	47
29	71	64
31	61	50
3,K,7		
1	70	75
3	86	89
5	75	80
7	130	135
9	68	70
11	50	51
13	78	80
15	98	96
17	109	108
19	90	89
21	39	41
23	71	70
25	71	70
27	82	82
3,K,9		
1	93	100
3	65	66
5	53	55
7	65	68
9	71	75
11	71	70
13	78	76
15	38	36
17	81	85
19	89	88
4,K,0		
0	270	266
2	472	487
4	47	55
6	295	307
8	327	335
10	254	251
12	46	47
14	114	114
16	177	178
18	46	47
20	34	25
22	24	29
24	100	107
26	11*	1
28	139	146
30	44	33
32	71	66
34	35	27
4,K,2		
2	533	540
4	24	26
6	225	234
8	125	130
10	313	317
12	90	92
14	175	183
16	58	63
18	243	245
20	25	19
22	148	155
24	17	24
26	97	85
28	24	22
30	51	47
32	23	15
34	105	91
4,K,4		
0	103	108
2	267	276
4	244	256
6	181	185
8	154	159
10	125	130
12	340	353
14	57	70
16	13	3
18	14	13
20	132	133
22	24	22
24	103	105
26	24	14
28	94	99
30	23	18
32	137	121
4,K,6		
2	126	128
4	22	23
6	140	148
8	45	47
10	38	42
12	55	57
14	100	102
16	21	12
18	146	146
20	22	21
22	60	59
24	13*	6
26	87	83
28	15*	6
4,K,8		
0	126	129
2	111	113
4	127	128
6	91	91
8	172	173
10	65	65
12	98	101
14	57	56
16	128	126
18	13*	7
20	63	60
22	16*	2
4,K,10		
2	96	97
4	14*	3
6	51	50
8	14*	9
10	75	80
12	15*	16
5,K,1		
1	407	403
3	293	295
5	152	153
7	311	307
9	222	227
11	159	163
13	152	157
15	21	22
17	233	238
19	140	146
21	58	56
23	32	31
25	123	119
27	119	115
29	43	49
31	19	15
33	114	100
35	35	28
5,K,3		
1	65	64
3	263	266
5	25	28
7	66	65
9	158	173
11	210	207
13	129	133
15	111	117
17	113	117
19	93	90
21	87	86
23	103	102
25	94	92
27	58	68
29	61	63
31	51	39
33	101	85
5,K,5		
1	86	90
3	207	216
5	98	105
7	90	81
9	126	130
11	161	165
13	109	114
15	96	98
17	124	119
19	104	107
21	107	105
23	98	95
25	41	36
27	81	78
29	67	63
31	27	34
5,K,7		
1	92	93
3	110	113
5	44	47
7	122	127
9	114	114
11	107	107
13	43	44
15	30	31
17	127	122
19	109	107
21	26	15
23	43	45
25	80	70
5,K,9		
1	111	112
3	59	60
5	30	23
7	86	91
9	52	51
11	61	58
13	46	49
15	47	42
17	59	63
6,K,0		
2	371	385
4	114	121
6	257	266
8	124	132
10	222	225
12	9*	2
14	155	158
16	103	108
18	195	199
20	126	138
22	90	98
24	11*	5
26	143	138
28	65	62
30	28	30
32	32	22
34	113	98
6,K,2		
0	194	194
2	168	167
4	438	438
6	245	245
8	80	78
10	74	77
12	264	287
14	43	48
16	80	84
18	68	67
20	102	109
22	36	43
24	106	110
26	53	49
28	71	79
30	40	38
32	122	106
34	37	19
6,K,4		
2	167	169
4	161	159
6	221	231
8	92	97
10	55	53
12	50	47
14	187	196
16	88	89
18	82	81
20	17	17
22	134	132
24	67	56
26	76	71
28	21	19
30	72	66
32	39	31
6,K,6		
0	37	39
2	56	58
4	239	252
6	91	91
8	77	75
10	56	63
12	189	193
14	55	58
16	92	88
18	51	47
20	95	95
22	30	18
24	97	92
26	29	22
28	63	67
6,K,8		
2	94	97
4	20	17
6	66	65
8	34	24
10	91	90
12	33	28
14	43	50
16	52	62
18	111	107
20	35	36
22	42	45
6,K,10		
0	65	63
2	45	39
4	160	157
6	31	37
8	65	64
7,K,1		
1	260	263
3	99	103
5	128	131
7	111	117
9	327	336
11	212	222
13	75	72
15	60	56
17	159	156
19	129	131
21	55	64
23	21	17
25	109	101
27	95	92
29	45	45
31	43	42
33	77	61
7,K,3		
1	220	222
3	145	148
5	197	212
7	157	158
9	164	167
11	182	191
13	110	118
15	115	118
17	165	157
19	143	145
21	76	70
23	35	29
25	107	101
27	95	90
29	48	49
31	66	61
7,K,5		
1	120	120
3	29	30
5	55	65
7	74	75
9	88	86
11	106	116
13	82	82
15	56	57
17	107	102
19	102	101
21	46	46
23	13*	20
25	69	63
27	79	73
29	52	48
7,K,7		
1	181	184
3	51	56
5	32	30
7	64	64
9	137	135
11	115	112
13	49	50
15	27	25
17	103	102
19	116	114
21	57	51
23	27	23
7,K,9		
1	82	76
3	79	81
5	47	52
7	49	44
9	114	108
11	107	106
13	16*	25
15	35	26
8,K,0		
0	362	366
2	75	75
4	314	318
6	22	17
8	69	84
10	71	77
12	226	232
14	32	34
16	133	143
18	31	36
20	187	192
22	27	27
24	131	135
26	21	26
28	28	22
30	34	25
32	111	102
8,K,2		
2	66	73
4	54	52
6	241	248
8	36	28
10	110	110
12	27	28
14	196	198
16	30	25
18	55	56
20	54	54
22	115	125
24	11*	7
26	117	114
28	56	46
30	106	101
32	29	15
8,K,4		
0	135	133
2	120	124
4	397	416
6	57	59
8	112	113
10	55	59
12	164	166
14	46	48
16	110	114
18	19	22
20	125	124
22	26	20
24	93	81
26	13*	18
28	54	51
30	16*	11
8,K,6		
2	112	117
4	28	25
6	159	163
8	10*	16
10	158	135
12	11*	10
14	136	140
16	62	57
18	67	62
20	27	20
22	115	111
24	35	35
26	104	92
8,K,8		
0	85	87
2	35	33
4	97	98
6	25	25
8	50	44
10	20	18
12	85	83
14	44	46
16	52	65
18	15*	5
20	84	83
8,K,10		
2	57	60
9,K,1		
1	255	260
3	54	54
5	39	46
7	94	99
9	273	275
11	156	154
13	130	140
15	131	139
17	125	127
19	101	100
21	89	91
23	62	57
25	87	79
27	92	87
29	55	48
31	73	60
9,K,3		
1	142	143
3	52	61
5	131	132
7	90	94
9	88	89
11	100	106
13	47	46
15	122	125
17	65	64
19	113	118
21	73	71
23	51	47
25	99	90
27	59	61
29	59	50
31	70	67
9,K,5		
1	135	137
3	34	40
5	97	102
7	84	88
9	107	109
11	120	126
13	60	59
15	69	64
17	62	61
19	110	104
21	57	66
23	13*	16
25	97	89
27	61	54
9,K,7		
1	142	138
3	11*	12
5	44	41
7	65	59
9	151	147
11	67	66
13	76	77
15	62	60
17	87	90
19	61	60
21	75	72
9,K,9		
1	86	82
3	34	38
5	42	38
7	50	51
9	129	126
11	52	55
10,K,0		
2	35	37
4	29	32
6	143	146
8	74	79
10	68	71
12	47	47
14	126	133
16	38	36
18	54	57
20	37	45
22	54	66
24	27	21
26	89	95
28	14*	6
30	80	76
10,K,2		
0	210	225
2	141	151
4	238	247
6	195	199
8	145	152
10	107	110
12	135	141
14	50	46
16	136	141
18	57	52
20	128	124
22	29	30
24	137	132
26	46	38
28	70	60
30	39	36
10,K,4		
2	93	97
4	98	104
6	170	174
8	65	69
10	79	82
12	31	33
14	194	191
16	54	53
18	12*	9
20	21	13
22	131	146
24	53	46
26	28	30
28	28	23
10,K,6		
0	94	94
2	53	55
4	126	131
6	93	91
8	59	62
10	68	69
12	76	77
14	45	48
16	90	89
18	42	40
20	76	75
22	15*	16
24	74	73
10,K,8		
2	94	90
4	14*	4
6	127	125
8	40	30
10	95	96
12	36	32
14	108	103
16	33	21
11,K,1		
1	194	197
3	145	151
5	135	141
7	134	189
9	120	123
11	115	117
13	71	70
15	117	117
17	108	112
19	89	95
21	53	49
23	66	69
25	75	75
27	99	83
29	62	55
11,K,3		
1	76	77
3	39	45
5	16	17
7	61	63
9	93	93
11	120	120
13	73	76
15	70	70
17	11*	6
19	47	40
21	97	97
23	92	88
25	41	34
27	40	32
29	80	71
11,K,5		
1	137	135
3	37	89
5	95	97
7	123	120
9	123	122
11	70	67
13	97	95
15	139	134
17	54	57
19	41	41
21	115	105
23	106	95
25	15*	22
11,K,7		
1	112	104
3	48	53
5	50	56
7	117	111
9	99	87
11	59	62
13	45	47
15	79	78
17	79	82
19	33	33
11,K,9		
1	95	94
3	25	13
5	17*	24
12,K,0		
0	140	141
2	74	79
4	9*	3
6	115	120
8	231	247
10	15	7
12	10*	3
14	10*	1
16	158	155
18	29	31
20	12*	6
22	13*	18
24	73	77
26	41	43
28	121	106
12,K,2		
2	159	171
4	70	59
6	117	120
8	50	54
10	116	125
12	61	64
14	133	135
16	71	67
18	103	106
20	55	54
22	137	133
24	13*	17
26	39	38
28	40	32
12,K,4		
0	145	149
2	69	68
4	67	74
6	101	100
8	149	149
10	60	59
12	148	148
14	36	34
16	47	48
18	33	32
20	89	90
22	30	22
24	72	73
26	37	30
12,K,6		
2	88	87
4	40	34
6	105	104
8	27	27
10	25	32
12	28	22
14	101	96
16	53	55
18	71	71
20	16*	10
12,K,8		
0	132	134
2	38	36
4	25	24
6	43	37
8	155	152
10	17*	22
12	29	33
13,K,1		
1	65	92
3	68	64
5	65	68
7	150	157
9	42	47
11	67	59
13	125	129
15	78	77
17	75	79
19	55	52
21	59	59
23	79	73
25	54	52
27	45	44
13,K,3		
1	82	84
3	160	162
5	91	94
7	103	105
9	56	53
11	70	71
13	132	129
15	73	71
17	44	43
19	23	20
21	95	85
23	114	103
25	46	40
13,K,5		
1	62	54
3	134	136
5	92	93
7	68	61
9	31	27
11	49	49
13	86	85
15	62	64
17	43	42
19	24	23
21	67	64
13,K,7		
1	78	61
3	50	43
5	39	37
7	121	122
9	68	71
11	23	24
13	65	56
15	80	78
14,K,0		
2	192	197
4	29	23
6	81	83
8	82	81
10	169	131
12	85	84
14	58	55
14,K,0		
16	19	11
18	159	151
20	13*	2
22	81	79
24	15*	14
26	90	79
14,K,2		
0	127	138
2	40	65
4	52	55
6	31	35
8	157	153
10	17	11
12	79	82
14	33	32
16	85	83
18	26	22
20	50	50
22	15*	19
24	58	54
14,K,4		
2	115	113
4	26	27
6	101	103
8	30	18
10	69	63
12	52	50
14	88	90
16	43	39
18	96	81
20	61	56
22	92	84
14,K,6		
0	156	157
2	35	34
4	42	38
6	45	40
8	173	164
10	26	25
12	84	77
14	27	17
16	48	94
15,K,1		
1	45	48
3	90	88
5	77	74
7	74	75
9	98	101
11	68	70
13	78	78
15	49	45
17	80	72
19	38	29
21	61	74
23	51	46
15,K,3		
1	26	24
3	128	121
5	162	156
7	73	78
9	21	15
11	70	68
13	124	122
15	98	95
17	54	61
19	34	37
21	84	78
15,K,5		
1	13*	14
3	61	58
5	97	97
7	64	65
9	44	37
11	40	34
13	89	81
15	70	70
17	16*	13
15,K,7		
1	54	55
3	70	69
5	53	56
7	45	37
16,K,0		
0	219	226
2	70	71
4	20	0
6	96	96
8	124	128
10	33	30
12	55	64
14	13*	14
16	91	85
18	14*	3
20	100	98
22	16*	21
16,K,2		
2	86	89
4	23	19
6	74	75
8	32	30
10	139	139
12	26	16
14	33	35
16	12*	11
18	109	98
20	38	37
16,K,4		
0	63	59
2	13*	6
4	96	100
6	32	29
8	52	50
10	31	25
12	51	62
14	14*	10
16	86	77
18	32	28
16,K,6		
2	86	85
4	15*	13
6	45	44
8	16*	3
10	135	127
17,K,1		
1	54	49
3	82	83
5	96	92
7	26	28
9	66	68
11	87	83
13	44	43
15	75	76
17	46	48
19	44	40
17,K,3		
1	13*	3
3	64	79
5	117	118
7	24	20
9	47	45
11	77	73
13	77	74
15	39	38
17	53	44
17,K,5		
1	42	39
3	77	72
5	130	115
7	33	43
9	29	24
11	88	84
18,K,0		
2	39	42
4	30	29
6	40	40
8	59	54
10	101	95
12	72	73
14	15*	10
16	25	18
18,K,2		
0	117	119
2	35	34
4	136	139
6	25	24
8	79	79
10	23	23
12	77	82
14	47	42
16	76	71
18,K,4		
2	81	74
4	15*	20
6	63	56
8	16*	9
10	121	111
19,K,1		
1	31	37
3	75	71
5	71	71
7	50	56
9	43	42
11	72	58
13	30	34
19,K,3		
1	59	56
3	81	71
5	63	53
7	63	55
9	53	47
20,K,0		
0	50	46
2	33	23
4	88	84
6	15*	0
8	83	80
20,K,2		
2	67	62
4	15*	11

[a] Columns are k, $10F_o$, and $10F_c$. F_o and F_c are on an absolute scale. Reflections marked with an asterisk are "unobserved."

TABLE IX

ATOMIC PARAMETERS OF $CaNa_2(CO_3)_2 \cdot 2H_2O$

Atom[a] D + B	Atom[a] C + S	x	y	z	B_{11}[b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca		0.0000	0.0000	0.0000	0.73 (8)	0.63 (8)	0.50 (8)	0.00 (1)	. . .	. . .
	Ca	0.0000	0.0000	0.0000	0.52 (2)					
Na		0.5653 (4)	0.1118 (3)	−0.0073 (12)	1.09 (16)	2.89 (23)	0.82 (16)	0.00 (2)	0.10 (19)	0.00 (2)
	Na	0.5653 (3)	0.1124 (1)	−0.0073 (7)	1.51 (4)					
C		0.0841 (8)	0.1355 (5)	−0.0072 (24)	0.84 (33)	1.05 (36)	0.55 (30)	0.00 (2)	−0.41 (36)	0.00 (4)
	C	0.0834 (5)	0.1362 (2)	−0.0090 (13)	0.63 (1)					
O(1)		0.1169 (7)	0.1975 (4)	−0.0121 (18)	1.76 (29)	0.81 (26)	1.24 (31)	−0.04 (2)	−0.43 (34)	0.02 (3)
	O(3)	0.1171 (4)	0.1982 (2)	−0.0119 (10)	0.98 (6)					
O(2)		0.0052 (6)	0.1161 (4)	0.1291 (15)	0.87 (25)	1.45 (29)	0.73 (27)	−0.01 (2)	0.23 (26)	0.00 (3)
	O(1)	0.0052 (4)	0.1161 (2)	0.1294 (10)	0.94 (6)					
O(3)		0.1297 (6)	0.0935 (4)	−0.1420 (15)	1.08 (27)	1.29 (27)	1.05 (33)	0.01 (2)	0.30 (28)	−0.02 (3)
	O(2)	0.1291 (4)	0.0934 (2)	−0.1419 (9)	1.05 (7)					
O(4)		0.6093 (7)	0.2432 (4)	0.0645 (18)	1.26 (28)	1.99 (34)	1.62 (36)	0.06 (2)	0.63 (29)	0.07 (3)
	O(4)	0.6088 (5)	0.2437 (2)	0.0625 (10)	1.39 (7)					

[a] D + B, this work; C + S, Corazza and Sabelli.[3] [b] Units of thermal parameters are $Å^2$; C + S give isotropic values.

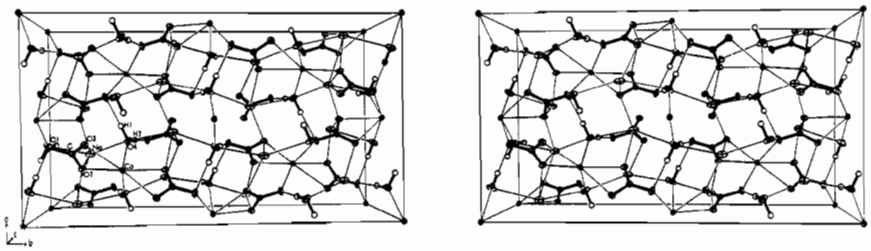


Figure 6.—Stereoscopic view along [001] of unit cell of $CaNa_2(CO_3)_2 \cdot 2H_2O$. The star indicates the origin of the coordinate system.

TABLE X
THE HYDROGEN POSITIONS IN $CaNa_2(CO_3)_2 \cdot 2H_2O$

	Electron density difference map			Least-squares[a] refinement			Calcd[b]			Corazza and Sabelli[3]		
	x	y	z	x	y	z	x	y	z	x	y	z
H(1)	0.54	0.26	0.05	0.56	0.27	0.07	0.53	0.26	0.04	0.527	0.265	0.034
H(2)	0.60	0.23	0.23	0.62	0.21	0.20	0.61	0.23	0.21	0.611	0.227	0.220

[a] The computed standard random errors are 0.001 in the x and y coordinates and 0.003 in the z coordinates. In the authors' opinion the systematic error is about an order of magnitude greater than this. [b] Calculated with imposed H_2O geometry (see text). These positions were used to calculate the interatomic distances.

Discussion of the Structure of $CaNa_2(CO_3)_2 \cdot 2H_2O$

The following description of the structure serves to amplify the briefer discussion given by Corazza and Sabelli and to relate the structure of $CaNa_2(CO_3)_2 \cdot 2H_2O$ to $CaNa_2(CO_3)_2 \cdot 5H_2O$.

General Features.—The structure (Figure 6) contains $Ca(CO_3)_2$ triplets in which the Ca, lying on a diad, bonds to the O(2)···O(3) edges of the two CO_3 groups. The Ca and the C and O(1) in each of the CO_3 groups lie nearly on a line. In contrast to $CaNa_2(CO_3)_2 \cdot 5H_2O$, the CO_3 groups are rotated about this axis to form a dihedral angle of 95.5°, and the triplets are linked into a three-dimensional network by Ca···O(1) bonds. The triplet axis is roughly normal to (010); thus its two carbons can lie in the sodium–carbon layers on either side of the calcium layer. Two water molecules, related by the diad, fill out the Ca coordination and hydrogen bond to CO_3 oxygens of neighboring triplets. The Na ions and the water molecules alternate in a column along $[01\bar{1}]$, but the Na is primarily bonded to a square of oxygens from four CO_3 groups.

The Calcium Environment.—As in $CaNa_2(CO_3)_2 \cdot 5H_2O$ and $CaCO_3 \cdot 6H_2O$,[13] the Ca ions lie on twofold axes. Their immediate environment in $CaNa_2(CO_3)_2 \cdot 2H_2O$ is summarized in Table XI and Figure 7. We have numbered the atoms in the CO_3 groups to correspond to those in $CaNa_2(CO_3)_2 \cdot 5H_2O$. The correspondence between our numbering scheme and that of Corazza and Sabelli is shown in Tables IX and X. The coordination of three CO_3 groups to Ca is a step toward the coordination in the calcite and aragonite phases of $CaCO_3$ where each oxygen in a CO_3 group is coordinated to two different Ca ions and the coordination of Ca is octahedral. In the calcite and aragonite phases of $CaCO_3$, no CO_3 group has two oxygens bonded to the same Ca. In $CaNa_2(CO_3)_2 \cdot 5H_2O$ and $CaNa_2(CO_3)_2 \cdot 2H_2O$, however, the Ca coordination comprises two CO_3 edges and four other oxygens. In $CaNa_2(CO_3)_2 \cdot 5H_2O$ these four oxygens are water molecules. In $CaNa_2(CO_3)_2 \cdot 2H_2O$ only two of these oxygens are in water molecules; the other two are CO_3 apexes (Figure 7). The two CO_3 groups coordinated to Ca have twisted 95.5° to allow close approach to Ca of the apexes of the other CO_3 groups. The Ca lies 0.1 Å away from the intersection of the planes of the CO_3 groups coordinated edgewise. The Ca···O distances are all in the normal range.

TABLE XI
Ca ENVIRONMENT IN $CaNa_2(CO_3)_2 \cdot H_2O$

Atoms	Distance, Å	Atoms	Distance, Å
Ca–O(1)	2.428 (9)	Ca–O(3)	2.536 (7)
Ca–O(2)	2.461 (7)	Ca–O(4)	2.483 (10)

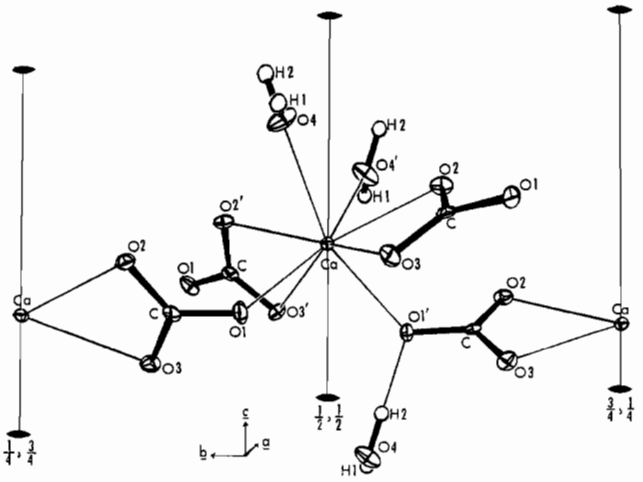


Figure 7.—The calcium ion environment in $CaNa_2(CO_3)_2 \cdot 2H_2O$.

The Carbonate Group.—The CO_3 group is planar and trigonal within experimental error with an average C–O distance of 1.286 Å. Its dimensions and environment are summarized in Figure 8 and Table XII. Oxygen O(1) is bonded primarily to Ca (2.428 Å) and forms two hydrogen bonds with neighboring water molecules. Oxygen O(2) is coordinated primarily to Ca (2.461 Å) and to the "chain" of Na ions (2.299

(13) B. Dickens and W. E. Brown, in preparation.

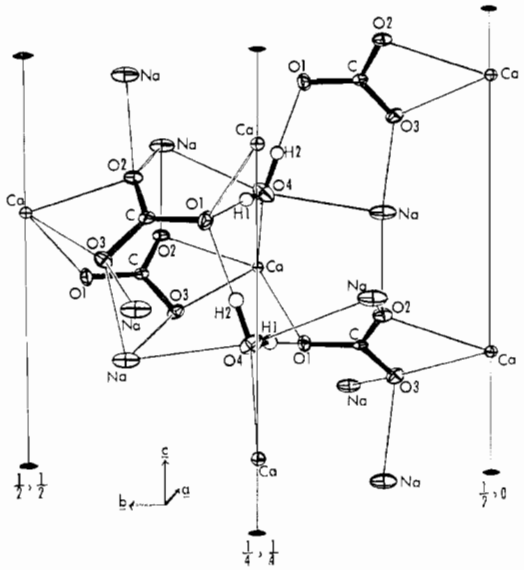


Figure 8.—The environments of the CO_3 anion and water molecule in $CaNa_2(CO_3)_2 \cdot 2H_2O$.

TABLE XII
CARBONATE DIMENSIONS AND ENVIRONMENT IN $CaNa_2(CO_3)_2 \cdot 2H_2O$

Atoms	Distance, Å
C–O(1)	1.300 (12)
C–O(2)	1.276 (14)
C–O(3)	1.281 (14)
O(1)–O(2)	2.237 (11)
O(1)–O(3)	2.236 (11)
O(2)–O(3)	2.209 (12)

Coordinated atoms	Angle, deg
O(1)–C–O(2)	120.5 (1.1)
O(1)–C–O(3)	120.1 (1.1)
O(2)–C–O(3)	119.4 (0.9)

O(1) environment

Atoms	Distance, Å
O(1)–Ca	2.428 (9)
O(1)–O(4)	2.865 (11)
O(1)–H(1)	1.91[a]
O(1)–O(4′)	2.716 (15)
O(1)–H(2′)	1.75[a]
O(1)–Na	2.945 (10)

O(2) environment

Atoms	Distance, Å
O(2)–Ca	2.461 (7)
O(2)–H(1)	2.53δ
O(2)–O(4)	3.118 (11)
O(2)–Na	2.299 (12)
O(2)–Na	2.302 (9)

O(3) environment

Atoms	Distance, Å
O(3)–Ca	2.536 (7)
O(3)–Na	2.351 (12)
O(3)–Na′	2.392 (9)
O(3)–O(1′)	3.023 (10)
O(3)–O(1″)	3.177 (10)

[a] The O···H distances were derived from the hydrogen positions, calculated with imposed geometry, given in Table X.

2.302 Å) formed above it by the *d* glide (Figure 9). Oxygen O(3) is bonded to Ca (2.536 Å) and to a "chain" of Na ions (2.351, 2.392 Å) formed below it by the *d* glide.

The Na Environment.—The Na coordination is summarized in Table XIII and Figure 9. Na is coordinated approximately octahedrally but primarily to O(2)- or O(3)-type oxygens of four surrounding

TABLE XIII
THE Na ENVIRONMENT IN $CaNa_2(CO_3)_2 \cdot 2H_2O$

Atoms	Distance, Å	Atoms	Distance, Å
Na–O(3)	2.351 (12)	Na–O(4)	2.722 (10)
Na–O(2)	2.299 (12)	Na–O(4′)	2.751 (10)
Na–O(2′)	2.302 (9)	Na–Na′	3.255 (8)
Na–O(3′)	2.392 (9)		

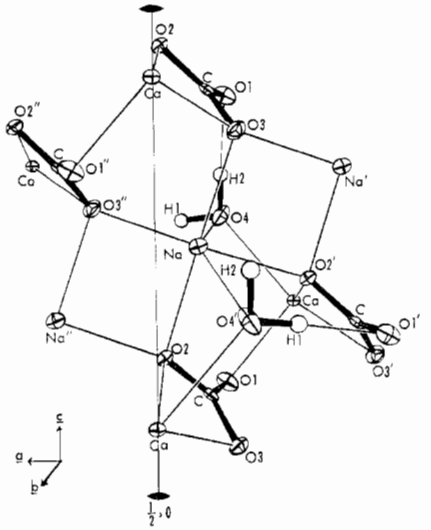


Figure 9.—The sodium ion environment in $CaNa_2(CO_3)_2 \cdot 2H_2O$.

triplets. The oxygens O(4) of the water molecules, which complete the coordination of Na, must be primarily coordinated to Ca, since the Na···O(4) distances of 2.751 and 2.722 Å are relatively large. Other things being equal, ~2.3 Å would be expected.

The Water Environment.—The environment of the water molecule is summarized in Table XIV and is shown in Figure 8. As in $CaNa_2(CO_3)_2 \cdot 5H_2O$, the shortest water-to-$CO_3$ oxygen distances, O(4)···O(1) and O(4)···O(1′), correspond to hydrogen bonds; the H(1)···O(1′) and H (2)···O(1) distances, 1.91 and 1.75 Å, respectively, are in the normal range and the bonds are nearly linear (*i.e.*, O–H···O bond angles are ~177°). The water molecule is coordinated to two Na ions (2.722 and 2.751 Å) in the alternating Na–H_2O chain parallel to $[01\bar{1}]$. In forming hydrogen bonds to oxygens of neighboring CO_3 groups, the hydrogens of the water lie in a plane which is approximately perpendicular to the plane formed by Na–O(4)–Na.

TABLE XIV
THE ENVIRONMENT OF WATER, H(1)–O(4)–H(2), IN $CaNa_2(CO_3)_2 \cdot 2H_2O$

Atoms	Distance, Å	Coordinated atoms	Angle, deg
O(4)–O(1)	2.716 (15)	O(1)–O(4)–O(1′)	108.7 (4)
O(4)–O(1′)	2.865 (11)	O(4)–H(1)–O(1′)	177
O(4)–O(2′)	3.135 (11)	O(4)–H(1)–O(2′)	121
O(4)–Ca	2.483 (10)	O(4)–H(2)–O(1)	177
O(4)–Na	2.722 (10)		
O(4)–Na′	2.751 (10)		
H(1)–O(1′)	1.91		
H(1)–O(2′)	2.53		
H(2)–O(1)	1.75		

Thermal Parameters.—The thermal motion of Ca is small and essentially isotropic. The largest components of Na and O(4) are roughly parallel to the line connecting the two atoms, where the bonding has been suggested to be weak. The major component of O(4) is also nearly perpendicular to the strong Ca···O(4) bond; that of Na is nearly normal to the four strong

bonds from Na to oxygens in adjacent CO_3 groups. The motions of the CO_3 atoms are fairly complex. They may be described as being approximately symmetrical about the O(1)–C–Ca–C′-O(1′) line, which is a pseudosymmetry element of the triplet.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

The Crystal Structure of Tris(hexafluoroacetylacetonato)-π-cyclopentadienylzirconium

BY M. ELDER

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The structure of tris(hexafluoroacetylacetonato)-π-cyclopentadienylzirconium, (π-C_5H_5)Zr($CF_3COCHCOCF_3$)$_3$, has been elucidated by single-crystal X-ray techniques and refined to a conventional residual of 6.1%. A total of 2009 observations above background, collected by counter methods, was used in the determination. The space group is monoclinic, $P2_1/n$, with a = 13.48 (2) Å, b = 23.03 (2) Å, c = 8.95 (1) Å, and β = 94° 52 (8′). The calculated density is 1.86 g cm^{-3} for four molecules per unit cell. The molecular complex exhibits pentagonal-bipyramidyl geometry. Five of the six coordinated oxygen atoms lie in an equatorial plane about the zirconium while the sixth oxygen and the π-cyclopentadienyl group occupy the two axial positions. The zirconium atom is displaced 0.39 Å from the equatorial plane toward the latter group. Two of the chelate rings exhibit folding of 4.5 and 8.4°, respectively, about the O···O line while the third ring, occupying axial and equatorial oxygen atom coordination positions, is planar. The two Zr–O distances in this ring differ by 0.10 Å.

Introduction

Nuclear magnetic resonance studies of high coordination number metal β-diketonates[1] have indicated that these complexes exhibit a considerable degree of lability in solution.[2-4] Even at low temperatures single-resonance lines in complexes such as Zr(acac)$_4$, Zr(acac)$_3$Cl,[5] Y(tfac)$_4^-$, and Y(hfac)$_4^-$ [4] indicate that a rapid intramolecular rearrangement averages the expected nonequivalent $-CH_3$ and $-CF_3$ environments. However, the presence of a π-cyclopentadienyl group in such complexes as (π-C_5H_5)Zr(acac)$_2$Cl[6] and (π-C_5H_5)-Zr(hfac)$_3$[7] influences the stereochemical nonrigidity of the β-diketone groups sufficiently to allow the observation of nonequivalent methyl proton and fluorine environments. The crystal structure determination of (π-C_5H_5)Zr(hfac)$_3$ was undertaken in order to provide some structural information toward the interpretation of this effect and to confirm the structural prediction based upon the nmr study.

(1) Abbreviations: acac, $CH_3COCHCOCH_3$; tfac, $CF_3COCHCOCH_3$; hfac, $CF_3COCHCOCF_3$.
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Experimental Section

Crystals of (π-C_5H_5)Zr($CF_3COCHCOCF_3$)$_3$ grown from acetone solution were kindly supplied by Mr. J. G. Evans. They were large, yellow parallelpipeds, many of which showed evidence of occluded solvent and air cavities under microscopic examination. Small, apparently flawless crystals were chosen for photographic purposes. Examination of Cu Kα radiation Weissenberg photographs of levels ($hk0$)–($hk2$) and Mo Kα radiation precession photographs of levels ($h0l$) and ($0kl$) showed 2/m Laue symmetry. The systematic absences ($0k0$) absent, k odd, and ($h0l$) absent, $h + l$ odd, indicated the monoclinic space group $P2_1/n$. This unconventional setting of space group C_{2h}^5-$P2_1/c$ was used throughout because of the near orthogonality of its axes. The general positions are: $\pm(x, y, z)$, $\pm(1/2 + x, 1/2 - y, 1/2 + z)$. Cell dimensions were determined from the precession photographs of the levels $0kl$ and $h0l$ taken with Mo Kα radiation (λ 0.71069 Å) at 26°. They were a = 13.48 ± 0.02 Å, b = 23.02 ± 0.02 Å, c = 8.95 ± 0.01 Å, and β = 94° 52′ ± 8′. The calculated density is 1.86 g cm^{-3} assuming four molecules per unit cell. An experimental density of 1.71 g cm^{-3} was determined using a pycnometer with water as the displacing liquid. The discrepancy between the two figures is not regarded as serious owing to the air cavities in the crystals which would be expected to cause a low experimental density for a bulk sample.

Intensity data were collected on a PAILRED fully automated diffractometer using a small single crystal mounted in a thin