[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Crystal Structure of Calcium–Barium Propionate

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The crystal structure of the double salt formed by the combination of two molecules of calcium propionate with one of barium propionate has been investigated by x-ray analysis.

Experimental

The salt was prepared by the method of A. Fitz and F. Sansoni.[1] The crystals used in the investigation were well formed, transparent octahedra and plates tabular on (111) faces. These were obtained from aqueous solutions by slow evaporation of the solvent; they were purified by fractional crystallizations. Analyses for free water, calcium and barium check the formula given by Fitz and Sansoni:[1] $Ca_2Ba(C_2H_5COO)_6$.

A water-cooled molybdenum target Coolidge tube and a hot cathode, water-cooled target demountable tube were employed. Molybdenum and silver targets were used in the latter.

The powder patterns were recorded on two cylindrical cameras, one having a radius of approximately 16.95 cm. and the other 3.505 cm. The crystal-to-plate distance used for single crystal photographs were 5 cm. for molybdenum radiation and 10 cm. for silver radiation. For monochromatic photographs, the molybdenum $K\alpha$ doublet was obtained by filtering with zirconium oxide. The crystal-to-plate distance was checked by means of spectral reflections from rock salt.

Laue photographs were taken along and at small angles to the [100], [110] and [111] axes. Molybdenum general radiation at 20 ma. and 48 k. v. peak, and silver general radiation at 35 ma. and 48 k. v. peak were used. Diffraction patterns were obtained of the crystal rotating around the [100], [110] and [111] axes. A series of overlapping 20° oscillations covering a 90° range about the [100] axis and a similar series of 5° oscillations covering a 45° range about the [100] axis were photographed. Also oscillation spectral reflections from a (111) face were photographed.

Structure Analysis

A precision of 0.5% in d/n values from powder patterns and 1% from single crystal photographs was obtained. Qualitative measurements of intensities were made by visual determination of photographic densities. These were used in all interpretations of diffraction data since the experimental results did not justify a more accurate procedure.

Lines on powder patterns were indexed by the usual methods. Laue photographs were indexed by aid of gnomonic projections and zone relationships. The oscillation and rotation photographs were indexed by the reciprocal lattice method.[2]

The external symmetry and optical properties of the crystals, as given by P. Groth and F. Sansoni,[1] were checked by Professor A. M. Brant of the Mineralogy Department of The Ohio State University. Data obtained from powder, Laue and rotation patterns verify the assignment of the crystal to the cubic system.

The length along an edge of the unit cell was found to be $a_0 = 18.3 \pm 0.1$ Å. This value was obtained from a rotation photograph taken about the [100] axis and from analyzed powder patterns; it was checked by the analysis of several Laue diagrams. An example of a calculation of a_0 from a powder pattern is given in Table I.

TABLE I

CALCULATION OF CELL SIZE FROM POWDER PHOTOGRAPH

First ten lines used because lines further from undeviated image could not be indexed unequivocally due to large cell size.

Obs. int.	hkl	$2L \pm$ 0.01 cm.	d_{hkl}	$(h^2 + k^2 + l^2)^{1/2}$	a_0(Å.)
10	220	3.70	6.51	2.83	18.4
10	222	4.56	5.28	3.46	18.3
10	400	5.22	4.62	4.00	18.4
8	331	5.74	4.20	4.36	18.3
10	440	7.49	3.23	5.66	18.3
6	620	8.37	2.89	6.32	18.3
4	551–711	9.42	2.57	7.14	18.4
4	642	10.02	2.42	7.48	18.2
2	733	10.80	2.24	8.18	18.3
1	660–822	11.34	2.14	8.48	18.2

The density of the crystals was determined to be 1.44 g./cc. at 27° by the Retgers suspension method. From this value of the density and the value of a_0 one finds the number of chemical molecules associated with the unit cell to be eight.

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[1] A. Fitz, *Ber.*, **13**, 1312 (1880); **14**, 1084 (1881); A. Fitz and F. Sansoni, *Z. Krist.*, **6**, 67 (1882).

[2] J. D. Bernal, *Proc. Roy. Soc.* (London), **A113**, 117 (1926).

The Bravais lattice of the crystal was found to be face centered cubic (Γ')[3,4] by criteria of layer line spacings on rotation photographs taken about the [100], [110] and [111] axes,[2] and abnormal spacings found in all photographs.[4]

Symmetry of Laue photographs taken along the [100] axis and along the [111] axis show that point groups T and T^h are very improbable.[4] Of the eleven space groups based on the Γ' lattice T_h^4, T_d^5, O_h^6, O_h^7 and O_h^8 are definitely eliminated by many observed reflections occurring on oscillation photographs. T^2, T_h^3, O^3 and O_h^5 are eliminated by consideration of associated equivalent positions and the number of cell elements.

T_d^2 and O^4 remain to be considered. Quartering of (100) planes was observed out to the twentieth order, thus it is extremely probable that O^4 is the correct space group.

If the crystals belong to point group T_d then they might be piezo-electrically active; if they belong to point group O they might be optically active. The crystals were not large enough to enable one to detect optical activity, if it were present.

The calcium and barium are assumed to exist in the crystal lattice as ions as also are the propionate groups. These assumptions are based on previous structure determinations and on the physical properties of the crystal such as high solubility in polar solvents, greater hardness than that of a purely organic crystal and decomposition at a fairly high temperature.

As a first approximation it was assumed that most of the intensity of the diffracted rays was due to scattering by the calcium and barium. Atomic form factors for barium were derived graphically from average values obtained by Thomas–Fermi[5] and Pauling–Sherman[6] distributions; those for calcium were obtained from the Hartree distribution.[7]

The diffraction data employed were taken from oscillation photographs. The spots used occurred on at least three different plates; they did not appear on high order layer lines, nor near the central image, nor were they due to planes reflecting at extremes of the oscillations. Intensities were made comparable from one plate to another by use of "standard spots" appearing on both plates. Calcium and barium were assumed to be in the various positions as given by the possible space groups; structure factors for these various positions were calculated. Calcium placed at positions given by 16-b[3] and barium at positions given by 8-f[3] gave the results listed in Table II. No other positions given by the possible space groups would give an agreement between calculated and experimental relative, qualitative intensities. Thus calcium and barium are definitely located in the crystal lattice. This arrangement of the calcium and barium ions is shown in Fig. 1.

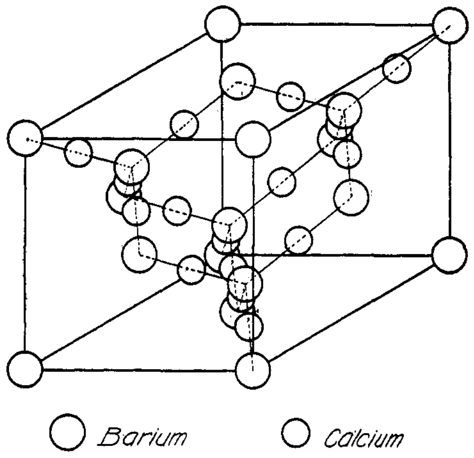

Fig. 1.—Unit cell showing locations of cations.

The barium ions lie in the positions of the "diamond lattice." The calcium ions form a tetrahedron around each barium; each calcium occupies a corner common to two such tetrahedra. The arrangement of these ions in the unit cell clearly shows the (111) planes characteristic of the crystal habit.

The diffraction effects exhibited on Laue photographs have a lower symmetry than that of the arrangement of barium and calcium ions (which symmetry is holohedral). This lower symmetry can only be due to the scattering of the propionate ions. O^4 requires at least an axis of 2-fold symmetry for the propionate ion. T_d^2 would require that each propionate group exhibit a plane of symmetry.

In addition to the fact that the data indicate O^4, T_d^2 does not give a plausible arrangement stereochemically. Hence we choose O^4 as the probable space group.

Since the diffraction effects arising from the

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[3] R. W. G. Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," Carnegie Institution of Washington, 2d ed., 1930.

[4] W. T. Astbury and K. Yardley, *Phil. Trans. Roy. Soc. London*, **224A**, 221 (1924).

[5] W. H. and W. L. Bragg, "The Crystalline State," G. Bell and Sons, Ltd., 1933, Vol. I, p. 328.

[6] Pauling and Sherman, *Z. Krist.*, **81**, 26 (1932).

[7] James and Brindley, *Phil. Mag.*, **12**, 81 (1931).

TABLE II

RESULTS OF CALCULATION OF THEORETICAL QUALITATIVE INTENSITIES FOR CALCIUM AND BARIUM AT POSITIONS INDICATED ABOVE

hkl	Obs. I	Calcd. I $\times 10^{-5}$	*hkl*	Obs. I	Calcd. I $\times 10^{-5}$	*hkl*	Obs. I	Calcd. I $\times 10^{-5}$
200	A.	0.0	666	W.	1.6	911	M. W.	5.3
400	W.	2.2				1111	W.	0.6
600	A.	0.0	1020	M. W.	4.2			
800	M.	18.3	480	W.	0.7	331	M. S.	18.5
1000	A.	0.0	1040	A.	.0	337	M. W.	6.7
1200	W.	.5	1240	M.	7.4	339	M. W.	4.6
1400	A.	.0	1060	M. W.	3.3	551	M. S.	8.8
1600	W.	4.2				553	W.	1.0
1800	A.	0.0	228	M. W.	6.0	771	W.	4.6
2000	..	.2	448	M. S.	12.3	991	W.	2.8
			662	W.	2.3			
220	S.	33.6	664	M.	6.3	359	W.	3.9
440	S.	34.6				791	W.	3.6
660	M.	7.0	268	M. W.	4.2			
880	M.	9.3	1024	M. W.	3.7	531	M.	12.4
			1028	W.	2.7	731	M. W.	1.0
222	M.	12.5	246	M.	7.8	1131	M.	3.6
444	W.	1.0				1151	M. W.	3.1
			511	W.	1.0			
			711	M.	8.8			

A. = absent. M. = medium. M. W. = medium weak. W. = weak. S. = strong. M. S. = medium strong.

propionate ion require a 2-fold axis of symmetry for this group, either the whole group is rotating or the –COO– portion must have a 2-fold axis. A simple calculation indicates that the moment of inertia of this group with any plausible arrangement of the oxygens is too large to permit rotation at room temperature. Hence the two oxygens must lie on the 2-fold axis or be crystallographically equivalent if the oxygens contribute appreciably to the x-ray scattering. The latter arrangement is, of course, the only tenable one.

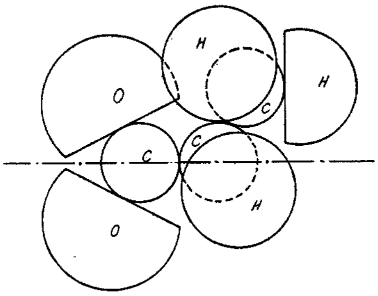

Fig. 2.—Model of propionate group.

If the C–C bond of the ethyl to the carboxyl group lies along the axis of the –COO– portion, the moment of inertia of this group also is too large to permit rotation at room temperature. As a result, we are forced to the conclusion that the principal portion of the contribution of the propionate ion to the x-ray diffraction effects is from the C–COO part (*i. e.*, the methyl carbon does not scatter appreciably and, of course, the hydrogens do not).

It is true that if the ethyl group is rotating about some figure axis, then it is possible that the 2-fold axis of the diffraction effects may be due to this portion of the propionate group and the scattering of the oxygens may not be appreciable. If this is so, then there is no evidence in these results for equivalence of the carboxyl oxygen. However, as has been pointed out, the moment of inertia of the ethyl group about its bond as an axis, is quite high and it is difficult to see how the group could rotate about any other axis. As a result the authors believe that the evidence is strongly in favor of the structure presented.

This arrangement of the oxygen also follows directly from the excellent work of Bragg and Morgan,[8] Zachariasen,[9] Pauling and Brockway[10] and Pauling and Sherman[11] on the scattering of substances containing the carboxyl group, from which data we construct a model of the propionate group as shown in Fig. 2.

In this model spherical carbon atoms of radius 0.77 Å., hydrogen domains in the form of spheri-

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(8) W. H. Bragg and G. T. Morgan, *Proc. Roy. Soc.* (London), **A104**, 437 (1923); G. T. Morgan and W. T. Astbury, *ibid.*, **A112**, 441 (1926).

(9) W. H. Zachariasen, *Phys. Rev.*, **45**, 755 (1934).

(10) L. Pauling and L. O. Brockway, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934).

(11) L. Pauling and J. Sherman, *ibid.*, **20**, 340 (1934).

cal segments of 1.1 Å. radius and a C–H distance of 1.08 Å.,[12] oxygen domains in the form of spherical segments of 1.35 Å. radius and C–O distance of 1.25 Å. are used with an angle between the two carbon–oxygen bonds of 126°.[9]

In O^4, the 2-fold axes of the propionate groups must be perpendicular to either the (100) planes or to the (110) planes. Models of both of these arrangements have been constructed using the above model for the propionate group. It was found impossible to get a satisfactory packing with the 2-fold axes perpendicular to the (110) planes. The other arrangement with the 2-fold axes perpendicular to the (100) planes (as given by the associated set of equivalent positions 48-c)[3] results in a very satisfactory packing of the ions.

This set of equivalent positions contains one variable parameter which must be evaluated in order to locate each group at the correct position along the corresponding axis.

The positions of the carboxyl groups have been fairly definitely fixed by consideration of the atomic and ionic radii, and the symmetry elements in the unit cell. The positions of the two ethyl carbons in each propionate group are then determined by the carbon bond directions, the size of the carbon atom, and the axis of symmetry along which the group must lie.

Figure 1 shows the locations of the calcium and barium ions in isometric projection. It is easily seen that the ions form four tetrahedra located in four of the eight octants of the unit cell.

Figure 3 shows a projection of one of these tetrahedra on a cube face of the cell. The packing of the oxygens with carboxyl carbons about the central barium ion is shown.

One ethyl group is shown in its approximate position along the 2-fold axis through the carboxyl carbon and the central barium ion.

The positions of the carboxyl carbons in the lattice may be obtained by substituting 0.16 for the variable parameter "u" in the associated set of forty-eight equivalent positions, 48-c.

It is interesting to note that, due to the surrounding oxygens, the barium ion has a coördination number of twelve and the calcium one of six.

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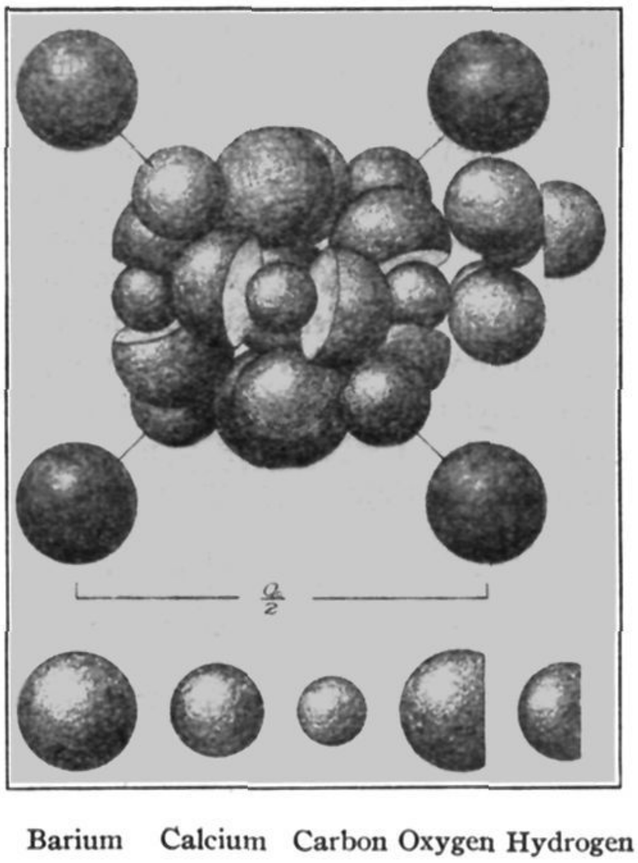

Fig. 3.—Packing of carboxyl groups about one barium ion, showing configuration of one propionate group.

Summary of Results

The density of calcium barium propionate was found to be 1.44 g./cc. at 27°.

The salt crystallizes in the cubic system with $a_0 = 18.3 \pm 0.1$ Å., the unit cell containing eight molecules of the double salt.

The crystal has the symmetry of O^4. This requires that the propionate group have a 2-fold axis of symmetry.

The positions of the barium and calcium ions are determined directly from the x-ray data and the approximate locations of the other atoms are inferred.

The resulting arrangement is a type of coördination structure of barium and calcium ions with the oxygens of the propionate groups.

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[12] E. Mack, Jr., THIS JOURNAL, 54, 2141 (1932).