

An X-ray examination of calcium formate.

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CALCIUM formate, $(\text{HCOO})_2\text{Ca}$, is soluble in cold water, from which it crystallizes by slow evaporation. Groth¹ gives the following data concerning the crystals of this substance:

Specific gravity (mean value) 2.019.

Orthorhombic bipyramidal; $a : b : c = 0.7599 : 1 : 0.4681$.

The molecular weight is 130.1. No definite cleavage has been observed, nor does twinning occur. There seems to have been some difference of opinion regarding the degree of symmetry. Originally the crystals were described as orthorhombic (holohedral) by J. C. Heusser in 1851, and this was followed by V. von Lang (1858) and A. Schrauf (1861). Later, however, Plathan² claimed to have observed unsymmetrical etch-figures which would prove the crystal to be bisphenoidal (like the strontium, barium, and lead formates), but Wagner³ found only etch-figures in accordance with what would be expected from bipyramidal symmetry.

The X-ray observations show clearly that the crystal-class is orthorhombic bipyramidal. Measurements were made using a Bragg spectrometer together with a Coolidge tube of rhodium anticathode. The experimental procedure was as follows. A well-formed crystal was chosen, measuring about 3 mm. each way (although one of smaller dimensions would have sufficed) and was set in plasticine on the crystal table with a zone-axis parallel to the spectrometer slits. On rotating the crystal about that axis, which is exactly at the centre of the spectrometer table, each of the planes in the zone comes in turn into such a position as to 'reflect' the homogeneous X-ray beam. These planes need not necessarily be crystal-faces, as the X-rays can readily penetrate the material and are not appreciably absorbed. By this means it is possible

¹ P. Groth, *Chem. Kryst.*, 1910, vol. 3, p. 12.² A. Plathan, [*Diss.*, Helsingfors, 1897], abstract in *Zeits. Anorg. Chem.*, 1898, vol. 18, p. 86.³ L. Wagner, *Zeits. Kryst. Min.*, 1911, vol. 50, p. 49.

to measure not only the spacings of the various planes, but the angles between them. The measurements of angles lead, of course, to the axial ratio given above and are otherwise used only for the identification of the planes. They are not, therefore, recorded. Planes in six different zones were found and their spacings are recorded in the table below. The spacing of the (100) plane is, of course, the length of the a axis, and when determined it could be substituted in the usual formula :

$$a \cdot b \cdot c \cdot \rho = n \cdot M \cdot m_H \cdot 10^{24},$$

where a, b, c are measured in Ångström units, ρ = density, n = number of molecules per unit cell, M = molecular weight, and m_H = mass of an atom of hydrogen.

Now, measurement gave $d_{(100)} = 10.16 \text{ \AA}$.

$$\text{Hence } \frac{(10.16)^3}{(0.7599)^2} \cdot 0.4681 \cdot 2.019 = n \cdot 130.1 \cdot 1.66.$$

Therefore $n = 7.94$ (i. e. 8).

Substituting $n = 8$ in the formula, it is possible to calculate a, b, c (i. e. $d_{(100)}, d_{(010)}, d_{(001)}$) and thence all the other spacings. These calculated values are compared with the observed values in the table below. The Roman numerals in the fourth column refer to the various orders of reflection.

Plane.	Spacing.		Comparative intensity of reflection.
	Calc.	Obs.	
(100)	10.19 Å.	10.16 Å.	II, III very small; IV very large.
(010)	13.41	*6.70	II mod. large; IV, VI, VIII mod. small.
(001)	6.27	*3.10	II very small.
(012)	3.05	3.04	I large.
(011)	5.68	5.64	I large; II mod. small.
(082)	2.56	2.53	I small.
(021)	4.58	*2.28	II large.
(081)	3.64	3.52	I small.
(041)	2.96	2.97	I small.
(120)	5.60	5.62	I very large; III large.
(280)	3.36	*1.66	II mod. small.
(340)	2.38	2.37	I small.
(110)	8.11	*2.02	IV very large.
(210)	4.76	*2.38	II large; IV mod. small.
(401)	2.40	2.33	I small.
(201)	3.95	3.94	I mod. large.
(802)	2.80	2.28	I mod. small.
(101)	5.34	5.32	I mod. large.
(208)	1.93	1.92	I large.
(102)	3.00	2.99	I small.

(continued)

Plane.	Spacing.		Comparative intensity of reflection.
	Calc.	Obs.	
(811)	2.91	2.90	I small.
(211)	3.79	3.81	I moderate.
(111)	4.96	4.96	I large.
(122)	2.76	2.71	I mod. large.
(141)	2.84	2.83	I mod. large.
(131)	3.43	3.44	I moderate.
(221)	3.41	3.40	I very large.
(331)	2.48	2.49	I moderate.

The spacings of the following planes (marked * in the table) were found to be abnormal: (010), (001), (021), (230), (110), (210). Of these, (110) showed a fourth order reflection only, thus appearing to possess a spacing one-fourth of the calculated size; the remainder gave a second order but no odd order reflections, their spacings thus appearing to be halved. Now although the spacings of (001) and (021) are apparently halved, those of (031) and (041) are of the full calculated value; hence no set of $\{0kl\}$ planes* is consistently halved. The halving of the (001) and (021) spacings must be due, not to the geometrical arrangement of the molecules in the cell, but to some accidental interference affecting these two planes only. Similarly, the (110) spacing cannot really be quartered, but is probably halved. The four planes (010), (230), (110), and (210) all belong to the zone $\{hk0\}$. The (100), (120), and (340), which also belong to this zone, show full spacings. Therefore only those planes in the zone $\{hk0\}$ are halved for which k is odd. This shows¹ that the crystal is based on the lattice Γ_0 and belongs to the space-group Q_h^8 . The eight molecules are therefore completely asymmetric in themselves. The class is certainly bipyramidal, since there are eight molecules in the cell and the Bravais lattice is Γ_0 . At present there is practically no evidence that would fix the exact positions of the molecules or of the atoms in the molecule. This may be possible when some other formates have been examined.

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¹ W. T. Astbury and K. Yardley, Phil. Trans. Roy. Soc. London, 1924, ser. A, vol. 224, p. 221. [Min. Abstr., vol. 2, p. 366.]