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A barium-iron-oxide with the perovskite structure.

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A perovskite-like structure having the composition $Ba_8Fe_8O_{21}$ has been reported as a result of an investigation of barium–iron–oxygen compounds (Erchak, Fankuchen & Ward, 1946). Later the Ba–Co–O system was examined and three new phases were found; $BaCoO_{2\cdot72}$, $BaCoO_{2\cdot31}$, and $BaCoO_{2\cdot23}$. The latter has the perovskite structure (Strauss, Fankuchen & Ward, 1951). Rare earth ferrites ($A^{3+}B^{3+}O_3^{6-}$) in which iron has a valence of 3^+ have been demonstrated (Geller & Wood, 1956). Barium manganite (Jonker & van Santen, 1950) and strontium cobaltite (Jonker & van Santen, 1953) have the perovskite structure with the transition metal in a valence state of $4^+(A^{2+}B^{4+}O_3^{6-})$.

In view of the above it was of interest to know if a reaction could be found that would produce a stoichiometric $BaFeO_3$ with the perovskite structure. Reacting various oxides, hydroxides and carbonates of barium and iron has to date failed to produce a compound with the perovskite structure. We have succeeded in obtaining a barium–iron–oxide with the perovskite structure by modifying the method of Clabaugh, Swiggard & Gilchrist (1956). This method was originally developed to produce a high purity barium titanate and consists in precipitating barium titanyl oxalate tetrahydrate followed by calcination.

The powder data listed in Table 1 were obtained with a Philips wide angle goniometer and Cu $K\alpha$ radiation. The data for cubic barium titanate are included in Table 1 as a basis for comparison. From this data it would follow that the new compound is isostructural with cubic $BaTiO_3$ and is stoichiometric $BaFeO_3$ with iron in a valence state of 4^+.

The deviation from the procedure of Clabaugh, Swiggard & Gilchrist consists in starting with a ratio of barium to iron of 1·5 to 1 instead of the ratio near 1 to 1 used with barium and titanium. The oxalate was precipitated at 50 °C. and calcined at 700 °C.

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Table 1. *Powder data*

	$BaFeO_3$				$BaTiO_3$		
			Intensities			Intensities	
hkl	*d*	a_0	Observed	Calculated	*d*	Observed	Calculated
100	4·012 Å	4·012 Å	8	14	4·017 Å	19	20
110	2·837	4·012	100	100	2·841	100	100
111	2·325	4·027	18	20	2·319	29	25
200	2·006	4·012	31	33	2·009	36	33
210	1·788	3·998	7	7	1·797	11	10
211	1·637	4·010	31	37	1·640	41	37
220	1·414	3·999	15	19	1·420	20	20
300, 221	1·338	4·014	4	3	1·339	6	4
310	1·272	4·022	11	16	1·270	16	16
311	1·211	4·016	7	6	1·211	8	8
222	1·159	4·015	4	6	1·160	7	7

Note: A Wilson Powder Camera was used to determine the *d* (Å) values.

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Histamine. — Preliminary X-ray studies of the crystalline free base.

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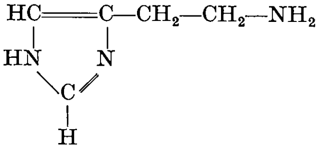

This is a report on the preparation and crystal structure of histamine free base ($C_5N_3H_9$) and is preliminary to the complete molecular structure determination of the free base. Neither the crystal structure nor the interplanar spacings of anhydrous histamine free base have been previously reported. However, the structure of the histamine iodine complex ($C_5N_3H_9 \cdot I_3$) has been reported by Cantrell (1961), and the *d*-spacings of histamine acid phosphate ($C_5N_3H_9 \cdot 2H_3PO_4$) have been published in the *X-ray Powder Data File.*

Since a satisfactory purification of histamine free base has never been reported, a procedure is described in detail for the preparation of single crystals suitable for X-ray crystallographic examination. A solution was prepared by dissolving 0·35 g. of histamine free base (Fisher reagent, lot 702338) in 100 ml. of boiling anhydrous benzene. Insoluble portions were separated, and the solution placed in a glass stoppered flask. This solution was then seeded with a small amount of histamine from the original sample, stoppered, and left to cool over night. Small, colorless, hygroscopic, needlelike crystals separated from the solution. These crystals were formed elongated along the *b* axis; they melted at 84 °C. with a sharp melting point. Elemental analysis gave the results: carbon, 51·90%; nitrogen, 38·50%; and hydrogen, 8·32%; corresponding to the formula $C_{4 \cdot 8}N_3H_9$. A solution of the above crystals in distilled water exhibited a molar absorptivity of 5380 liters per mole per cm. at a wave length of 2080 Å. This corresponds to the value of 4940 liters per mole per cm. reported by Butler (1961) for histamine as received from the supplier. The present authors believe 5380 liters per mole per cm. is the better value because of the purification procedure.

Crystals of approximately 3 mm. length and 0·1 mm. width were selected for the Weissenberg and rotation photographs. These were individually mounted and sealed in Lindemann glass tubes. The Weissenberg photographs were taken with the *b* axis perpendicular to the incident Co $K\alpha$ X-radiation. The reciprocal lattice was constructed, and from this the unit cell was shown to be monoclinic.

Two techniques were employed in the preparation of samples used for powder pattern analysis. (1) A small crystal was ground by the mechanical agitation of a glass rod inside a Lindemann glass tube of 0·2 mm. diameter and 0·01 mm. wall thickness and then sealed. (2) A sample of molten histamine was allowed to cool slowly in a similar tube and crystallize into a polycrystalline solid. The same patterns were obtained from both sample preparation techniques; however, the polycrystalline solid was preferred because the smaller crystallite size gave more uniform diffraction rings in the photographs. The powder patterns were taken with a 143·25 mm. diameter camera using Cu $K\alpha$ radiation. Intensities and *d*-spacings of the observed lines are listed in Table 1.

The equatorial and first layer Weissenberg photographs showed the crystals to be monoclinic and gave the values of *a*, *c*, and β listed in Table 2. To determine the true value of the *b* axis, trial calculations of the *d*-spacings were performed using multiples of the value observed from the rotation photographs. These *d*-spacings were then compared with the *d*-spacings observed from the powder patterns. By this procedure the *b* axis was found to be 15·28 ± 0·02 Å or twice that initially observed in the rotation photographs; thus the systematic absence of all reflections with *k* equal to an odd interger occur. The volume of the unit cell is 605·6 Å^3. If four molecules are assumed present in each unit cell, the calculated density is 1·22 grams per cubic centimeter. A density of 1·20 grams per cubic centimeter was determined by flotation in ethylbenzoate–iodobenzene mixtures. For a monoclinic cell containing four molecules and systematic absences when *k* is an odd integer, the indicated space group is $P2_1/m$.

Table 1. *Powder data for anhydrous histamine free base*

hkl	*I*(exp.)	*d*(exp.)	*d*(calc.)
100	*m*	7·042	6·998
120	*vw*	5·175	5·159
021	*s*	4·453	4·446
$12\bar{1}$	*vs*	4·168	4·156
040	*vw*	3·814	3·819
140	—	—	3·379
$20\bar{1}$	*s*	3·343	3·354
220	—	—	3·181
041	*w*	3·140	3·131
$22\bar{1}$	*vw*	3·088	3·061
$14\bar{1}$	*w*	3·021	3·023
201	—	—	2·659
$12\bar{2}$	*vw*	2·635	2·615
$24\bar{1}$	—	—	2·597
240	*vw*	2·577	2·580
022	—	—	2·573
221	*vw*	2·524	2·510
$14\bar{2}$	*w*	2·258	2·256
122	—	—	2·250
$10\bar{3}$	—	—	1·883
222	*vw*	1·875	1·873
023	*w*	1·776	1·773

Table 2. *Lattice constants for anhydrous histamine free base*

$a = 7·23 \pm 0·06$ Å
$b = 15·28 \pm 0·02$ Å
$c = 5·63 \pm 0·09$ Å
$\beta = 104·5 \pm 0·4°$
$V = 605·6 \pm 1·6$ Å^3
D(exp.) = 1·20 g.cm.$^{-3}$
D(calc.) = 1·22 g.cm.$^{-3}$
Z = 4 molecules per unit cell

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