

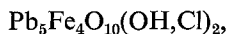
# Hematophanite, a derivative of the perovskite structure<sup>1</sup>

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**SUMMARY.** Hematophanite, ideally  $\text{Pb}_4\text{Fe}_3\text{O}_8\text{Cl}$ , is tetragonal, space group  $P4mm$ , with  $a = 3.92$  and  $c = 15.31$  Å. The crystal structure, which has been refined to an  $R$ -factor of 9.1%, may be described as an interlayering of perovskite-like units with a cesium chloride or, alternatively, a nadorite-like unit. The nadorite-like part consists of a double layer of  $\text{PbO}_4\text{Cl}_4$  distorted square antiprisms. Iron atoms are in 6-fold (tetragonal bipyramidal) and 5-fold (square pyramidal) coordination.

HEMATOPHANITE was first described by Johansson (1928) as a tetragonal mineral with unit-cell parameters  $a = 7.82$  and  $c = 15.26$  Å. A chemical formula,



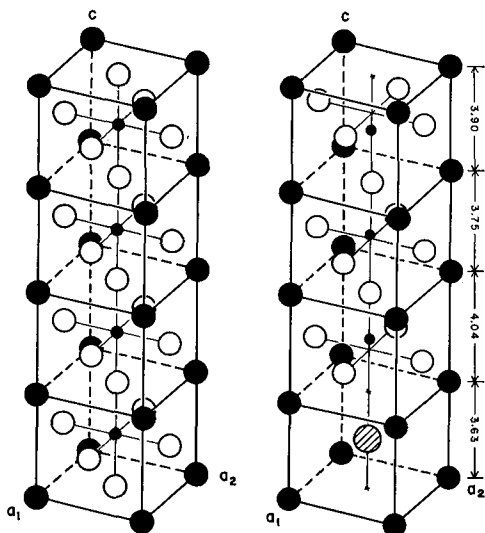
was derived on the basis of two chemical analyses. Rouse (1971a) found hematophanite to be tetragonal, diffraction symmetry  $P4/mmm$ , with  $a = 3.92$  and  $c = 15.31$  Å. An idealized crystal structure consisting of four perovskite-like subcells stacked congruently, one on top of the other, was proposed along with the chemical formula  $\text{Pb}_4\text{Fe}_4\text{O}_9(\text{OH},\text{Cl})_2$ .

*Structure determination.* A specimen of hematophanite from Långban, Sweden, was kindly supplied by Dr. P. B. Moore of the University of Chicago. A tabular cleavage fragment of dimensions  $0.19 \times 0.12 \times 0.02$  mm was mounted on an automated single-crystal diffractometer. Using Weissenberg equi-inclination geometry, pulse-height analysis, and monochromated  $\text{Mo-K}\alpha$  radiation, the intensities of 235 non-equivalent reflections were measured. These were then corrected for Lorentz, polarization, and absorption effects. Solution and refinement of the structure were carried out using the method of least-squares in the IBM 360 programme SFLSQ5 written by C. T. Prewitt. Scattering factors for  $\text{Pb}^+$  were obtained from Cromer and Waber (1965),  $\text{Fe}^{3+}$  and  $\text{Cl}^{3-}$  from Doyle and Turner (1968), and  $\text{O}^-$  from the International Tables for X-ray Crystallography (1962), assuming half-ionized atoms. Anomalous dispersion corrections for Pb, Fe, and Cl were taken from Cromer (1965). All reflections were equally weighted.

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Determination of the structure was begun using the 'four perovskite cell model' (fig. 1), which has the formula  $\text{Pb}_4\text{Fe}_4\text{O}_{12}$  (this structure is purely hypothetical since the stoichiometric perovskite  $\text{Pb}^{2+}\text{Fe}^{3+}\text{O}_3$  does not exist). As noted in Rouse (1971a), structure factors calculated assuming space group  $P4mm$  gave the lowest  $R$ -factor. All further calculations were therefore done in this space group. Refinement of atomic site occupancy factors and isotropic temperature factors indicated two deviations from



FIGS. 1 and 2: FIG. 1 (left). The four perovskite cell model. The large and small dark circles represent Pb and Fe atoms, respectively. Open circles are O atoms. FIG. 2 (right). The structure of hematophanite with the origin at a Pb atom. The shaded circle represents a Cl atom.

the ideal model. Firstly, the three anion sites in the first subcell (the lowermost one in figs. 1 and 2) were vacant. Secondly, the Fe site at coordinates  $1/2, 1/2, 1/8$  was either partially occupied by an Fe atom or fully occupied by an atom of somewhat lower atomic number, probably chlorine. The latter alternative was chosen for two reasons. As shown in fig. 2, the length of the first subcell is  $3.63 \text{ \AA}$ , which is just the diameter of a  $\text{Cl}^-$  ion (radius  $1.81 \text{ \AA}$ ). The other subcells are significantly larger. In addition, this is the only available site in the structure capable of accommodating the large  $\text{Cl}^-$  ion.

The existence of these deviations was confirmed by electron density syntheses, which consistently showed less electron density at  $1/2, 1/2, 1/8$  than at the other Fe sites. Difference syntheses confirmed this and also indicated essentially no electron density at the three anion sites in the first subcell. This leaves the subcell with a composition  $\text{PbCl}$  as opposed to  $\text{PbFeO}_3$  for the others. The supercell shown in fig. 2 has the composition  $\text{Pb}_4\text{Fe}_3\text{O}_8\text{Cl}$ . This polar structure is consistent only with the initially assumed space group,  $P4mm$ . The other possibilities ( $P4/mmm$ ,  $P422$ ,  $P\bar{4}2m$ ,  $P\bar{4}m2$ ) would require the equivalence of the  $\text{PbCl}$  subcell and the uppermost perovskite-like subcell.

The final  $R$ -factor is  $9.1 \%$  for all reflections or  $6.1 \%$  if the unobserved ones are excluded.<sup>1</sup> Table I contains a list of atomic parameters. Table II is a list of interatomic distances with standard errors calculated using the variance-covariance matrix for atomic coordinates. Due to the predominant influence of the lead atoms on the structure factors, the anion positions could not be determined with high accuracy. There are also strong interactions among the temperature factors of Cl, Fe(1), Fe(2), and

<sup>1</sup> A table of observed and calculated structure factors has been deposited in the library of the Department of Mineralogy, British Museum (Natural History), London, SW 7.

Fe(3), and it was therefore necessary to hold these parameters constant at arbitrary values during the refinement.

*Chemical composition.* The chemical formula  $\text{Pb}_4\text{Fe}_3\text{O}_8\text{Cl}$  found in the structure analysis may be compared to that calculated from the average chemical analysis of Johansson (1928). The calculated unit-cell contents are: Pb 3.59, Na 0.13, K 0.04, Ca 0.05,  $\text{Fe}^{3+}$  3.01, Mg 0.02, Mn 0.05,  $\text{Fe}^{2+}$  0.05, Ti 0.01, O 8.49, H 0.88, Cl 0.67, or  $(\text{Pb,Na,K,Ca})_{3.81}(\text{Fe}^{3+},\text{Mg,Mn,Fe}^{2+},\text{Ti})_{3.14}\text{O}_{8.49}\text{H}_{0.88}\text{Cl}_{0.67}$ . Johansson's analysis has been checked qualitatively with the electron probe, which indicates the presence of

TABLE I. *Atomic parameters in hematophanite (standard errors in parentheses)*

Atom	x	y	z	B ( $\text{\AA}^2$ )	Atom	x	y	z	B ( $\text{\AA}^2$ )		
Pb(1)	1a	0	0	0.000*	0.42	Cl	1b	1/2	1/2	0.121(9)	2.0
Pb(2)	1a	0	0	0.237(1)	0.95	O(1)	2c	1/2	0	0.339(5)	1.4
Pb(3)	1a	0	0	0.501(1)	0.56	O(2)	1b	1/2	1/2	0.478(6)	0.86
Pb(4)	1a	0	0	0.745(1)	1.1	O(3)	2c	1/2	0	0.607(8)	4.0
Fe(1)	1b	1/2	1/2	0.363(2)	0.50	O(4)	1b	1/2	1/2	0.747(7)	1.6
Fe(2)	1b	1/2	1/2	0.619(5)	0.50	O(5)	2c	1/2	0	0.915(4)	0.29
Fe(3)	1b	1/2	1/2	0.870(4)	0.50						

\* Coordinate arbitrarily fixed at 0.000 in the absence of an inversion centre.

TABLE II. *Interatomic distances in hematophanite (standard errors in parentheses)*

Pb(1)-	{ 4 O(5)	2.35(3) $\text{\AA}$	Fe(2)-	{ 4 O(4)	1.96(12) $\text{\AA}$
	{ 4 Cl	3.33(7)		{ 4 O(3)	1.97(1)
Pb(2)-	{ 4 O(1)	2.51(5)		{ 4 O(2)	2.15(11)
	{ 4 Cl	3.29(7)	Fe(3)-	{ 4 O(4)	1.88(12)
Pb(3)-	{ 4 O(3)	2.56(7)		{ 4 O(5)	2.08(3)
	{ 4 O(2)	2.79(1)	O(1)-	{ 4 O(1)	2.77
	{ 4 O(1)	3.16(6)		{ 2 O(2)	2.90(9)
Pb(4)-	{ 4 O(4)	2.77(1)	O(2)-	4 O(3)	2.80(10)
	{ 4 O(3)	2.87(8)	O(3)-	{ 4 O(3)	2.77
	{ 4 O(5)	3.26(5)		{ 2 O(4)	2.89(11)
Fe(1)-	{ O(2)	1.76(10)	O(4)-	4 O(5)	3.24(10)
	{ 4 O(1)	2.00(2)	O(5)-	4 O(5)	2.77

only Pb, Fe, and Cl. Oxygen was not determined due to instrumental limitations. Assuming that the observed density of  $7.70 \text{ g/cm}^3$  is in error and normalizing to four Pb, the formula becomes (including the minor elements)  $\text{Pb}_{4.00}\text{Fe}_{3.30}\text{O}_{8.91}\text{H}_{0.92}\text{Cl}_{0.70}$  or very nearly  $\text{Pb}_4\text{Fe}_{10/3}\text{O}_8(\text{OH})\text{Cl}_{2/3}$ . The excess OH relative to  $\text{Pb}_4\text{Fe}_3\text{O}_8\text{Cl}$  can be explained, in part, as  $\text{OH}^-$  substituting for  $\text{Cl}^-$ . This would also account for the apparent deficiency in the latter element. The source of the remaining OH and the excess Fe is still uncertain, however. It may be due simply to an error in the chemical analysis, as the hematophanite in the author's specimen is extensively altered. In any case, there is probably some ionic substitution in hematophanite and the formula  $\text{Pb}_4\text{Fe}_3\text{O}_8\text{Cl}$  must be regarded as idealized.

*Structure and bonding.* The structure of hematophanite may be described in two different ways in order to bring out its relationships to other phases. In fig. 2 it appears as a combination of four subcells. Three of these have a distorted perovskite structure (composition  $\text{PbFeO}_3$ ) and one, a distorted cesium chloride structure (composition  $\text{PbCl}$ ). Two of the perovskite-like subcells have a vacant oxygen site and their composition is more properly written  $\text{PbFeO}_{2.5}$ .

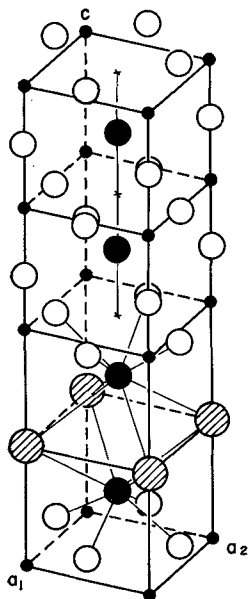


FIG. 3. The structure of hematophanite with the origin at an Fe atom.

If the origin of the supercell is now moved from a lead to an iron atom, the result is the structure shown in fig. 3. The upper half of the supercell now consists of two stoichiometric perovskite-like cells. The lower half is a double layer of distorted  $\text{PbO}_4\text{Cl}_4$  square antiprisms having the atom sequence O–Pb–Cl–Pb–O, i.e.  $\text{Pb}_2\text{O}_2\text{Cl}$ . This double-layered unit is very similar to one found in nadorite,  $\text{PbSbO}_2\text{Cl}$  (Sillén and Melander, 1941) and perite,  $\text{PbBiO}_2\text{Cl}$  (Gillberg, 1961). Nadorite is orthorhombic, but there is a synthetic polymorph  $(\text{Pb,Sb})_2\text{O}_2\text{Cl}$ , which is tetragonal with  $a = 3.90$  and  $c = 12.28\text{Å}$ . These three compounds are, in turn, isostructural with a member ('type  $X_1$ ') of a large group of mixed bismuth oxides and oxyhalides (Structure Reports, 1947–8). Many members of this series also contain perovskite-like units of composition  $\text{BiTiO}_3$ . An example is the phase  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (Aurivillius, 1949).

The presence of nadorite-like layers in hematophanite explains its perfect  $\{001\}$  cleavage. Lead–chlorine bonds in this layer will be considerably weaker than cation–oxygen bonds in the rest of the structure. Since the layers are parallel to  $(001)$ , cleavage should occur parallel to this plane breaking the lead–chlorine linkages. The presence of a perfect cleavage in the mineral nadorite parallel to the layers supports this analysis. A similar situation involving the preferential breaking of lead–chlorine bonds in layers of  $\text{PbO}_4\text{Cl}_4$  antiprisms occurs in diabolite (Rouse, 1971*b*).

In hematophanite, the atoms Pb(3) and Pb(4) are coordinated by cubo-octahedra of twelve oxygen atoms since they occur in the cubic closest-packed perovskite subcells. Pb(1) and Pb(2) of the nadorite layer are coordinated by distorted square antiprisms of 4 O+4 Cl (Pb–O = 2.35, 2.51 Å and Pb–Cl = 3.33, 3.29 Å). Disregarding the Pb–Cl bonds, each Pb atom is located at the apex of a low pyramid, which has a square of O atoms as its base. This  $\text{PbO}_4$  configuration is very common and indicates a high degree of covalency in the Pb–O bond (Dickens, 1965). On the other hand, the Pb–Cl distances are consistent with ionic bonding. In the perovskite-derivative, diabolite ( $\text{Pb}_2\text{Cu}(\text{OH})_4\text{Cl}_2$ ), the distances Pb–OH = 2.48 Å and Pb–Cl = 3.22, 3.43 Å are comparable to those in hematophanite.

A further analogy to the diabolite structure is the square pyramidal coordination of the small cation. Fe(1) and Fe(3) are in 5-fold square pyramidal coordination by

oxygen and lie 0.4 and 0.7 Å, respectively, above the basal planes of the pyramids. This can be seen in fig. 2. Reference to fig. 1 and table I shows that it is the oxygen rather than the iron atoms that are displaced from their ideal positions in the four perovskite cell model. When oxygen atoms at  $1/2, 1/2, 0$  and  $1/2, 1/2, 1/8$  in fig. 2 are removed, the  $\text{Fe}^{3+}$  ions are less screened from the  $\text{Pb}^{2+}$  than they were in octahedral coordination. A positional adjustment is now necessary to minimize cation-cation repulsions. This is accomplished by small shifts in the oxygen positions to place the  $\text{Fe}^{3+}$  ions inside the square pyramids. By contrast, no vacancies occur in the anion polyhedron around  $\text{Fe}(2)$ . It remains in distorted octahedral (tetragonal bipyramidal) coordination and lies essentially in the equatorial plane of the bipyramid.

TABLE III. *Observed and predicted shape parameters of the antiprisms\**

General symbol	HSM	MFP	Pb(1) antiprism	Pb(2) antiprism
$l$	1.22	1.26	1.31	1.33
$s$	1.22	1.19	1.18	1.15
$l/s$	1	1.06	1.11	1.16
$\theta$	59.3°	57.3°	56.4°	54.4°

\* Definitions of the shape parameters are given by Hoard and Silverton (1963).

*Description of the antiprism.* The shape of an antiprismatic coordination polyhedron may be described by the parameters  $l$  and  $s$  or, alternatively, by the angle  $\theta$  (Hoard and Silverton, 1963). Hoard and Silverton calculate these parameters for two theoretical models: the ideal Hard Sphere Model (HSM) and the Most Favourable Polyhedron (MFP), which is the hard sphere configuration slightly distorted to minimize ligand-ligand repulsions. In table III the theoretical parameters for both models are compared to the observed ones for the antiprisms in hematophanite. The correspondence between the observed and MFP parameters is rather good. This is true despite the large difference in size between the oxygen and chlorine ligands and the presence of a non-bonding electron pair in the valence shell of  $\text{Pb}^{2+}$ . A similar calculation has also been made for the  $\text{PbO}_4\text{Cl}_4$  antiprism in diabolite (Rouse, 1971b).

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