

Tableau 7. Distances intermoléculaires (< 3,5 Å)

La convention suivante est utilisée: C(18)—C(71) $3/\sqrt{100}$ signifie que C(18) est en position équivalente 1 et C(71) en position 3 translattée d'une maille suivant $-x$. Les positions équivalentes sont:

(1) x, y, z	(5) $\frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{4} + z$
(2) $-x, -y, \frac{1}{2} + z$	(6) $\frac{1}{2} + y, \frac{1}{2} - x, \frac{3}{4} + z$
(3) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{4} - z$	(7) $y, x, -z$
(4) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{4} - z$	(8) $-y, -x, \frac{1}{2} - z$

Les liaisons hydrogène sont marquées d'une astérisque.

C(6)—O(82)	$2/11\bar{1} \equiv 7/001$	3,463 (12)
C(7)—O(83)	$5/1\bar{1}\bar{1}$	3,445 (13)
C(8)—O(83)	$5/1\bar{1}\bar{1}$	3,417 (14)
C(18)—C(71)	$3/\sqrt{100}$	3,399 (17)
C(55)—O(81)	$4/1\bar{1}\bar{1}$	3,387 (11)
C(56)—O(81)	$4/1\bar{1}\bar{1}$	3,424 (11)
C(57)—O(80)	$4/1\bar{1}\bar{1}$	3,342 (11)
C(59)—O(11)	$5/1\bar{1}\bar{0}$	3,406 (11)
C(71)—O(11)	$8/220$	3,389 (18)
C(72)—O(80)	$4/1\bar{1}\bar{1}$	3,340 (11)
N(1)—O(80)*	$4/1\bar{1}\bar{1}$	2,895 (9)
N(4)—O(82)*	$2/11\bar{1} \equiv 7/001$	2,915 (9)
N(51)—O(81)*	$2/11\bar{1}$	2,901 (8)
N(54)—O(81)*	$4/1\bar{1}\bar{1}$	2,933 (9)
O(80)—O(81)*	$1/000$	2,807 (9)
O(81)—O(83)*	$3/\bar{1}\bar{1}\bar{1}$	2,733 (12)
O(82)—O(83)*	$3/\bar{1}\bar{1}\bar{1}$	2,817 (12)
O(82)—O(83)*	$6/\bar{1}\bar{1}\bar{1}$	2,817 (12)

Les auteurs remercient les Professeurs J. Toussaint et A. Denoël pour l'intérêt qu'ils ont porté à ce travail.

Références

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & SAUNDERSON, C. P. (1967). NRC Crystallographic Programs for the IBM 360 System, National Research Council, Ottawa, Canada.
- CRUICKSHANK, D. W. J. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, édité par R. PEPINSKY, J. M. ROBERTSON & J. C. SPEAKMAN. Oxford: Pergamon Press.
- DECLERCQ, J. P., GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1973). *Acta Cryst.* **A29**, 231–234.
- DIDEBERG, O., DUPONT, L. & ANGENOT, L. (1975). *Acta Cryst.* **B31**, 1571–1575.
- DIDEBERG, O., LAMOTTE-BRASSEUR, J., DUPONT, L., CAMPSTEYN, H., VERMEIRE, M. & ANGENOT, L. (1977). *Acta Cryst.* **B33**, 1796–1801.
- GUILHEM, J. (1974). *Acta Cryst.* **B30**, 742–747.
- JOHNSON, C. K. (1971). *ORTEP II*. Oak Ridge National Laboratory Report ORNL-3794, revised.
- KOCH, M. H. J. (1974). *Acta Cryst.* **A30**, 67–70.
- MAIN, P. (1970). Program for the reduction of diffractometer data, Univ. of York, England.
- PREWITT, C. T. (1967). *SFLS* program, State Univ. of New York, Stony Brook, Long Island, New York 11790, USA.
- WENKERT, E. & BRINGI, N. V. (1959). *J. Amer. Chem. Soc.* **81**, 1474–1481.

Acta Cryst. (1977). **B33**, 1807–1811

The Crystal Structure of Stenhuggarite

BY ALESSANDRO CODA,* ALBERTO DAL NEGRO, CESARE SABELLI† AND VITTORIO TAZZOLI

Centro di Studio per la Cristallografia Strutturale del Consiglio Nazionale delle Ricerche, Istituto di Mineralogia dell'Università, Via Bassi 4, 27100 Pavia, Italy

(Received 19 October 1976; accepted 20 November 1976)

Stenhuggarite, $\text{CaFeSbAs}_2\text{O}_7$, is tetragonal, with $a = 16.144$ (3), $c = 10.706$ (2) Å, space group $I4_1/a$, $Z = 16$. The structure was refined to $R = 0.041$ for 1446 independent reflexions. Ca displays a coordination polyhedron halfway between a cube and a square antiprism. The other coordination polyhedra are (ψ means that a vertex is occupied by an electron lone pair): Sb, ψ -trigonal bipyramid; As, ψ -tetrahedron; Fe, trigonal bipyramid; their bond lengths and angles, and their distortions from regularity are in accordance with the valence shell electron pair repulsion model (VSEPR). Two kinds of anion units are present, not sharing O atoms between them: one, $(\text{As}_4\text{O}_8)^{-4}$, consists of eight-membered rings; the other, $(\text{AsSbO}_5)^{-4}$, is formed of helices $-\text{O}-\text{Sb}-\text{O}-$ with $-\text{OAsO}_2$ side groups. This study shows that the formula is $\text{Fe}^{\text{III}}\text{Ca}[\text{As}^{\text{III}}\text{O}_2/\text{As}^{\text{III}}\text{Sb}^{\text{III}}\text{O}_5]$.

Introduction

Stenhuggarite is a rare mineral found in an association, filling small pockets in haematite ore. According to

* Address: Istituto di Cristallografia dell'Università, Via Bassi 4, 27100 Pavia, Italy.

† Address: Istituto di Mineralogia dell'Università, Via Lamar-mora 4, 50121 Firenze, Italy.

Moore (1970), an electron microprobe analysis gave the composition $\text{Ca}_{1.00}\text{Fe}_{0.98}\text{Sb}_{1.00}\text{As}_{2.06}\text{O}_{7.76}$ which suggests the chemical formula $\text{CaFe}^{\text{III}}\text{Sb}^{\text{V}}\text{As}_2^{\text{III}}\text{O}_y$ ($y = 7.5$), but also $\text{CaFe}^{\text{III}}\text{Sb}^{\text{III}}\text{As}_2^{\text{III}}\text{O}_y$ ($y = 7$) is possible, since close agreement with analysis cannot be expected.

This study has been undertaken to establish the correct valence states and to contribute to the crystal chemistry of the natural arsenites.

A preliminary account of the structure, based on photographic data, has been presented (Coda, Dal Negro, Sabelli & Tazzoli, 1973).

Experimental

Morphology and general properties of stenhuggarite have been studied by Moore (1970); the crystals are brilliant orange and usually pseudo-octahedral. Table 1 lists the crystal and diffraction data.

The intensities were measured by ω -scans on a Philips PW 1100 computer-controlled four-circle diffractometer with Mo $K\alpha$ radiation monochromatized by a graphite crystal. All 2038 intensities for the unique portion of reciprocal space with $\sin \theta/\lambda \leq 0.7035$ were measured; 1446 reflexions with $I > 2\sigma(I)$ were considered observed; the remaining 592 reflexions were ignored as they had $I_i - 2\sqrt{I_i} < I_b$, where I_i is the intensity in counts s^{-1} measured at the top of the scan, and I_b is the mean intensity in counts s^{-1} of both background measurements during a preliminary run of 5 s at each end of the scan.

The background counting time t' at each end of the scan was $t' = (I_b/I_i)t/2$, where t is the scan time and I_i is the mean intensity in counts s^{-1} during the scan. The intensities were corrected for Lorentz and polarization factors and for absorption ($\mu R = 0.9$), assuming the crystal to be roughly spherical with radius 0.005 cm.

Structure determination and refinement

The structure was solved by symbolic addition with *LSAM* (Germain & Woolfson, 1968). 314 normalized structure factors with $|E| \geq 1.20$ and the phases generated by the maximum consistency set allowed the calculation of an E map that gave the positions of all heavy atoms. Successive Fourier syntheses yielded the coordinates of all O atoms. The initial R of 0.20 was reduced to 0.068 after three least-squares cycles carried out with a modified Busing, Martin & Levy (1962) *ORFLS* program. Scattering factors for neutral Sb, As,

Table 1. *Crystal and diffraction data*

CaFeSbAs₂O₇, $M_r = 479.5$
 Tetragonal, $a = 16.144(3)$, $c = 10.706(2)$ Å, $V = 2790.3$ Å³
 Space group: $I4_1/a$
 $Z = 16$, $D_c = 4.56$, $D_m = 4.63(5)$ g cm⁻³ (Moore, 1970)
 $F(000) = 2208$
 Crystal dimensions (the sample was roughly an ellipsoid): $0.098 \times 0.098 \times 0.139$ mm
 Radiation: Mo $K\alpha$, $\lambda = 0.71069$ Å, graphite monochromator
 $\mu = 167$ cm⁻¹
 Scan angular range: $\Delta\omega = 1.5^\circ$; scan speed: 0.032° s⁻¹
 θ range: $2-30^\circ$; maximum $(\sin \theta)/\lambda$: 0.7035
 Number of measured independent reflexions: 2038 (592 of which were considered unobservably weak)

Table 2. *Atomic coordinates*

In this and all subsequent tables, estimated standard deviations are shown in parentheses. The figures given in the last column (B_H in Å²) represent the equivalent isotropic thermal parameters (Hamilton, 1959). Positional parameters are $\times 10^4$.

	<i>x</i>	<i>y</i>	<i>z</i>	B_H
Sb	3265.8(4)	4269.7(4)	162.0(6)	0.70
As(1)	3850(1)	2981(1)	-2615(1)	0.56
As(2)	3973(1)	3146(1)	-7039(1)	0.41
Fe	2373(1)	2575(1)	-4916(1)	0.41
Ca	3493(1)	4388(1)	-4768(2)	0.48
O(1)	3272(4)	3154(4)	-1225(7)	1.08
O(2)	2527(4)	4845(4)	-1007(6)	0.59
O(3)	2468(4)	3448(4)	806(6)	0.82
O(4)	3049(4)	3100(4)	-3738(6)	0.96
O(5)	3020(4)	3283(4)	-6317(6)	0.70
O(6)	4201(4)	4008(4)	-2883(7)	1.13
O(7)	4544(4)	3389(4)	-5612(6)	0.82

Fe and O (Hanson, Herman, Lea & Skillman, 1964) were used. At this stage anisotropic thermal parameters were introduced. After two cycles, weighted according to the experimental $\sigma(F_o)$ derived from counting statistics, R was reduced to 0.041 and R_w to 0.035 for the 1446 reflexions.

The final positions and equivalent isotropic temperature factors are given in Table 2.*

Structure description and discussion

1. Oxidation numbers and chemical formula

The structure determination leads to an unambiguous choice of chemical formula: CaFe^{III}Sb^{III}As₂O₇. As a small excess of O is suggested by the electron microprobe analysis, the final difference map was inspected, but no residual O atoms were found. Thus, Fe as the ferric cation and As and Sb in the form of arsenite and antimonite are the relevant oxidation states.

2. Coordination polyhedra

The Sb, As and Fe coordination polyhedra and their contacts are shown in Fig. 1, those of Ca in Fig. 2. Bond lengths in polyhedra are given in Table 3. Table 4 shows synoptically the kind of contacts between any sharing pair of polyhedra.

* Lists of structure factors, anisotropic thermal parameters and the analysis of the thermal ellipsoids have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32341 (14 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

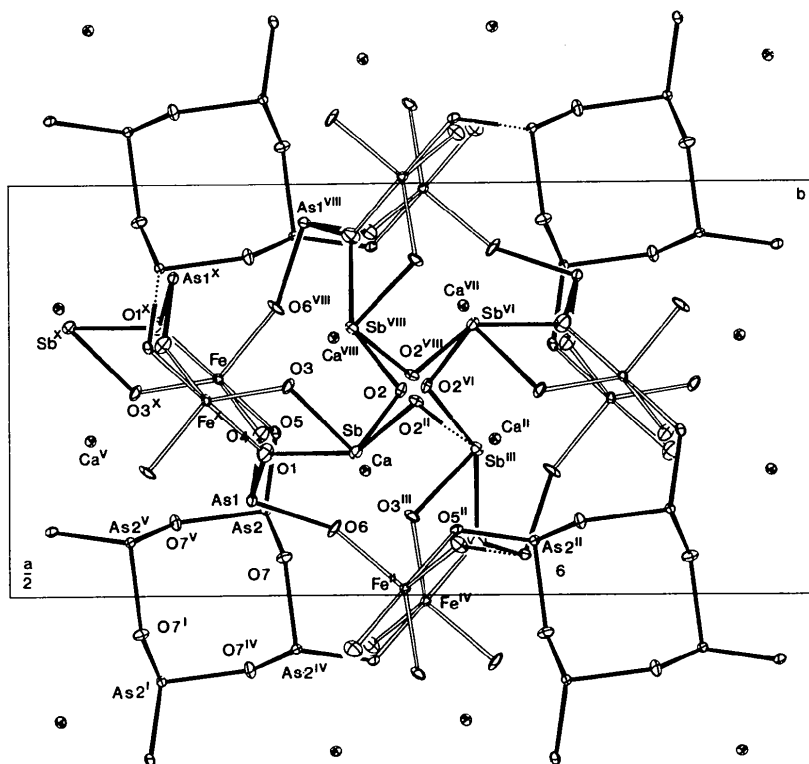


Fig. 1. ORTEP (Johnson, 1965) plot of the crystal structure of stenhuggarite, showing the Sb, As and Fe coordination polyhedra and their contacts. See Table 3 for symmetry code. The bonds terminated by dotted lines refer to atoms which are equivalent to those shown in the figure by translation along *c*.

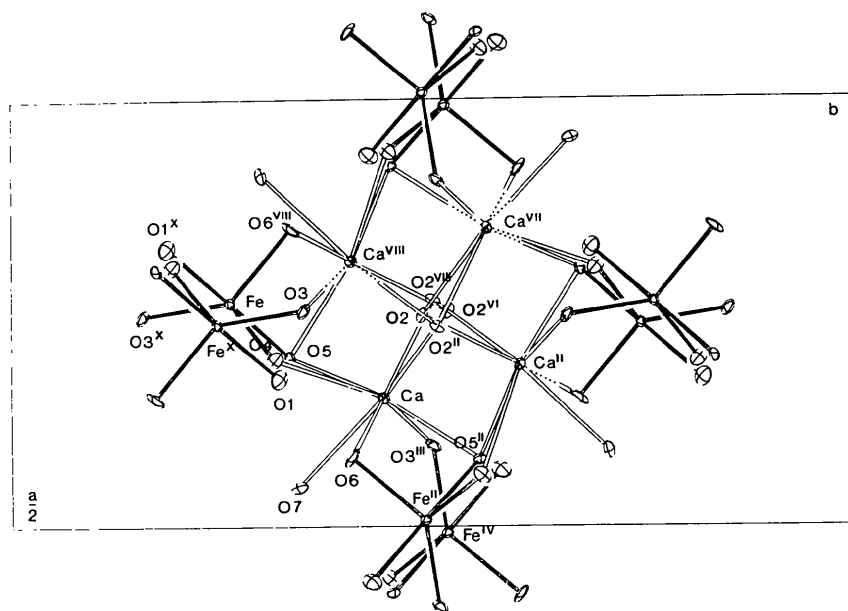


Fig. 2. Projection comparable to that of Fig. 1, showing the Ca coordination polyhedra and their contacts.

Table 3. *Interatomic distances* (Å)

Symmetry code			
(i)	$1 - x, \frac{1}{2} - y, z;$	(vi)	$\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$
(ii)	$\frac{3}{4} - y, \frac{1}{4} + x, \frac{1}{4} + z;$	(vii)	$\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$
(iii)	$\frac{3}{4} - y, \frac{1}{4} + x, z - \frac{3}{4};$	(viii)	$y - \frac{1}{4}, \frac{3}{4} - x, z - \frac{1}{4}$
(iv)	$\frac{1}{4} + y, \frac{3}{4} - x, -z - \frac{3}{4};$	(ix)	$y - \frac{1}{4}, \frac{3}{4} - x, \frac{3}{4} + z$
(v)	$\frac{3}{4} - y, x - \frac{1}{4}, -z - \frac{5}{4};$	(x)	$\frac{1}{2} - x, \frac{1}{2} - y, -z - \frac{1}{2}$
Sb—O(1)	2.335 (7)	Fe—O(1 ^x)	1.990 (7)
Sb—O(2)	1.962 (7)	Fe—O(3 ^x)	1.925 (6)
Sb—O(2 ⁱⁱ)	2.121 (7)	Fe—O(4)	1.871 (7)
Sb—O(3)	1.974 (6)	Fe—O(5)	2.156 (7)
		Fe—O(6 ^{viii})	1.888 (6)
As(1)—O(1)	1.778 (7)	Ca—O(2 ^{vi})	2.451 (7)
As(1)—O(4)	1.775 (7)	Ca—O(2 ^{viii})	2.480 (7)
As(1)—O(6)	1.776 (6)	Ca—O(3 ⁱⁱⁱ)	2.438 (7)
		Ca—O(4)	2.460 (7)
		Ca—O(5)	2.551 (7)
As(2)—O(5)	1.736 (7)	Ca—O(5 ⁱⁱ)	2.397 (7)
As(2)—O(7)	1.826 (7)	Ca—O(6)	2.399 (7)
As(2)—O(7 ^v)	1.801 (6)	Ca—O(7)	2.509 (7)

Table 4. *Contacts between sharing pairs of polyhedra*

For symmetry code see Table 3.

From	to	by	From	to	by
Sb	Sb ⁱⁱ	O(2 ⁱⁱ)	Fe	Sb ^x	O(1 ^x)—O(3 ^x)
	Sb ^{viii}	O(2)		As(1)	O(4)
As(1)	O(1)	O(1)		As(1 ^{viii})	O(6 ^{viii})
	Fe ^x	O(1)—O(3)		As(1 ^x)	O(1 ^x)
	Ca ⁱⁱ	O(2)		As(2)	O(5)
	Ca ^{vii}	O(2)—O(2 ⁱⁱ)		Ca	O(4)—O(5)
	Ca ^{ix}	O(2 ⁱⁱ)—O(3)		Ca ^v	O(3 ^x)
				Ca ^{viii}	O(5)—O(6 ^{viii})
As(1)	Sb	O(1)	Ca	Sb ⁱⁱⁱ	O(2 ^{vi})—O(3 ⁱⁱⁱ)
	Fe	O(4)		Sb ^{vi}	O(2 ^{vi})—O(2 ^{viii})
	Fe ⁱⁱ	O(6)		Sb ^{viii}	O(2 ^{viii})
	Fe ^x	O(1)		As(1)	O(4)—O(6)
	Ca	O(4)—O(6)		As(2)	O(5)—O(7)
				As(2 ⁱⁱ)	O(5 ⁱⁱ)
As(2)	As(2 ^{iv})	O(7)		As(2 ^{iv})	O(7)
	As(2 ^v)	O(7 ^v)		Fe	O(4)—O(5)
	Fe	O(5)		Fe ⁱⁱ	O(5 ⁱⁱ)—O(6)
	Ca	O(5)—O(7)		Fe ^{iv}	O(3 ⁱⁱⁱ)
	Ca ^v	O(7 ^v)		Ca ⁱⁱ	O(2 ^{viii})—O(5 ⁱⁱ)
	Ca ^{viii}	O(5)		Ca ^{viii}	O(2 ^{vi})—O(5)

The following description of coordination polyhedra refers to specific atoms of the unit cell (as defined in Table 2), or their symmetry-equivalents (as labelled in Table 3).

Sb^{III} coordination

The coordination of Sb is conveniently described with a five-vertex polyhedron: starting from the Sb coordinates of Table 2, the four vertices are O(1), O(2), O(2ⁱⁱ) and O(3), the fifth is a lone pair of electrons. According to the VSEPR model, a ψ -trigonal bipyramid (ψ -tbp) is obtained (Gillespie, 1970).

An empirical rule of the VSEPR model is that lone pairs prefer equatorial positions: then in stenhuggarite one of the equatorial positions of the ψ -tbp around Sb is occupied by a lone pair; the other two equatorial positions are O(2) and O(3); the axial vertices are O(1) and O(2ⁱⁱ).

Another rule of the model is that a lone pair is more spread than a shared one: accordingly, distortions of the ψ -tbp occur, with contraction of the interatomic axial and equatorial angles from the ideal values of 180 and 120° respectively: in stenhuggarite the axial angle O(1)—Sb—O(2ⁱⁱ) is 151.0° and the equatorial O(2)—Sb—O(3) is 98.3°.

Lastly, according to the model, and in agreement with data on Sb^{III} ψ -tbp coordination reported in the literature, the axial Sb—O distances (Table 3) are longer than the equatorial; the mean values are: axial, 2.228, equatorial, 1.968 Å. The agreement with the figures of Tapscott, Belford & Paul (1969) is close.

The ψ -tbp shares the vertices O(2) and O(2ⁱⁱ) with two neighbouring Sb^{viii} and Sbⁱⁱ ψ -tbp's; thus infinite helical chains —Sb—O—Sb—O— are formed running along 4₁.

As^{III} coordination

Two different sets of equivalent As atoms, As(1) and As(2), exist in the structure. Both display the same kind of ψ -tetrahedral coordination, in close agreement with the VSEPR model, but their role in the network is quite different. O(1), O(4) and O(6) are vertices of the As(1) ψ -tetrahedron, and O(5), O(7) and O(7^v) those of the As(2); the fourth vertex of both is occupied by an electron lone pair. As(1) belongs to the same anion unit to which Sb also pertains: it will be described later. The As(2) tetrahedron shares O(7) and O(7^v) with two neighbouring As(2^v) and As(2^v) tetrahedra, which again repeat this sort of sharing, so that both end up in the same As(2) tetrahedron through their vertices O(7^{iv}) and O(7) respectively. Thus eight-membered rings arise that close about inversion axes 4.

Fe^{III} coordination

The coordination polyhedron of Fe^{III} is a trigonal bipyramid, slightly distorted: axial angle, 173.7; equatorial angles 109.3, 119.9, 130.1°. With Fe coordinates of Table 2 as a reference, this tbp is formed of the axial O(1^x), O(5) and equatorial O(3^x), O(4), O(6^{viii}).

Ca coordination

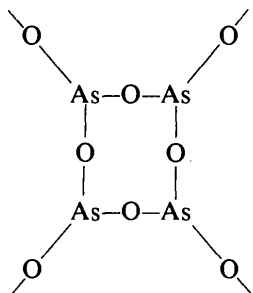
Ca, with coordination number eight, displays a polyhedron halfway between a square antiprism and a cube; its quasi-square bases are formed of O(3ⁱⁱⁱ), O(5ⁱⁱ), O(6), O(7) and O(2^{vi}), O(2^{viii}), O(4), O(5). Helical chains

run along the 4_1 axes by edge-sharing of the Ca antiprism with two neighbouring antiprisms Ca^{ii} and Ca^{viii} , by $\text{O}(2^{\text{viii}})\text{—O}(5^{\text{ii}})$ and $\text{O}(2^{\text{vi}})\text{—O}(5)$ respectively, and so on.

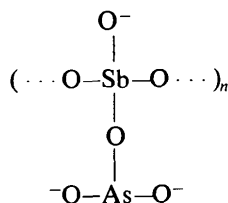
3. Anion and cation units

The crystal structure is conveniently described in terms of anionic units and cations linked to them.

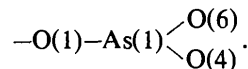
Two distinct anion units are present, not sharing any O atoms between them. One, $(\text{As}_4\text{O}_8)^{4-}$, consists of the As(2) eight-membered rings connected to the cations Fe^{3+} and Ca^{2+} by sharing O(5); an axis 4 cuts perpendicularly the centre of each ring.



The other, $(\text{AsSbO}_8)^{4-}$, is composed of helices $\text{—Sb—O}(2)\text{—Sb—}$ that run along the screw axes 4_1 ,



with side groups $\text{—O}(3)$ and



The O atoms of each helix are shared with Ca^{2+} , those of the side groups are linked to Fe^{3+} and Ca^{2+} . There is no direct connexion between the cations Fe^{3+} , whereas the Ca^{2+} coordination polyhedra form helical chains developing along 4_1 .

The chemical formula can be written as $\text{Fe}^{\text{III}}\text{Ca}[\text{As}^{\text{III}}\text{O}_2/\text{As}^{\text{III}}\text{Sb}^{\text{III}}\text{O}(5)]$. According to IUPAC rules the chemical name of this compound is calcium iron(III) *cyclo*-dioxoarsenate(III)(1-) *catena*[trioxoarsenate(III)] dioxoantimonate(III) (4-).

We are indebted to P. B. Moore (Department of the Geophysical Sciences, University of Chicago) who provided a sample of stenhuggarite.

References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
- CODA, A., DAL NEGRO, A., SABELLI, C. & TAZZOLI, V. (1973). *Atti Congresso Italo-Jugoslavo di Cristallografia*, Trieste, pp. 88–91.
- GERMAIN, G. & WOOLFSON, M. M. (1968). *Acta Cryst.* **B24**, 91–96.
- GILLESPIE, R. J. (1970). *J. Chem. Educ.* **47**, 18–23.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
- MOORE, P. B. (1970). *Ark. Miner. Geol. Stockh.* **5**, 55–62.
- TAPSCOTT, R. E., BELFORD, R. L. & PAUL, I. C. (1969). *Coord. Chem. Rev.* **4**, 323–359.