Liebauite, $Ca_3Cu_5Si_9O_{26}$:
A new silicate mineral with 14er single chain

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Dedicated to Prof. Dr. F. Liebau on the occasion of his 65th birthday

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Abstract. The new calcium copper silicate liebauite has been found in cavities of a mudstone xenolith from the Sattelberg scoria cone near Kruft in the Eifel district, Germany. It occurs as bluish-green transparent crystals with a vitreous lustre and a Mohs hardness between 5 and 6. The analytical formula for liebauite based on 26 oxygen atoms is $Ca_{2.99}Cu_{4.91}Si_{9.05}O_{26}$, the idealized formula is $Ca_3Cu_5Si_9O_{26}$, and the structural formula $Ca_6Cu_{10}\{1B, 1_\infty^1\}[^{14}Si_{18}O_{52}]$. The mineral is monoclinic, space group $C2/c$ with $a = 10.160(1)$, $b = 10.001(1)$, $c = 19.973(2)$ Å, $\beta = 91.56(1)°$, $V = 2028.7$ Å^3 and $Z = 4$. The strongest lines in the X-ray powder diffraction pattern are [$d(\text{Å})$, I, hkl] 7.13(60) (110), 6.70(70) ($11\bar{1}$, 111), 3.58(40) (220), 3.12(90) (131, 131), 3.00(100) (116, 312), 2.45(60) (226), 2.41(70) (226), 1.78(50) (440). Liebauite is biaxial positive with $\alpha = 1.722$, $\beta = 1.723$, and $\gamma = 1.734$ ($\lambda = 589$ nm). Determination and refinement of the crystal structure led to a conventional R value of 0.046 for 818 observed reflections

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and 86 refined parameters. Liebauite is the first known natural 14er loop branched single chain silicate. Si—O distances in the five crystallographically different tetrahedra vary between 1.569 and 1.677 Å with an average of 1.624 Å.

Occurrence and origin

About ten years ago Dr. H. E. Künzel (Dormagen/Germany) found an unusual xenolith bearing a number of copper minerals in a pit at the Sattelberg near Kruft in the Eifel, Germany. Apart from tenorite, volborthite, calciovolborthite and cuprorivaite a few very small, bluish-green crystals, which could clearly be distinguished from the pure blue cuprorivaite crystals, were observed in the xenolith.

The Sattelberg near Kruft (TK 25 Bl. 5510 Neuwied) is a former scoria cone in the Quaternary volcanic field of the Eastern Eifel. The top of the volcano has been removed by the mining of the scoria during the last 100 years but the massive agglutinates in the centre of the pit have not been removed completely. These agglutinates contain some xenoliths which were subjected to a very high grade thermal metamorphism changing the mineral paragenesis of the xenoliths to tridymite, cristobalite, mullite, cordierite, osumilite and many other minerals. The copper minerals were found in a brown to black xenolith about 0.5 m in size. The originally fine-sandy to argillaceous sedimentary rock fragment was strongly heated and partially molten before it solidified vitreously. The hornfels-like rock shows many very small vesicles which are mostly empty and only rarely contain some secondary minerals. Minerals dominating in filled fissures are sanidine, clinopyroxene, and cristobalite, sometimes mullite, cordierite, pseudo-brookite, haematite, Cu-minerals like tenorite, volborthite, calciovolborthite, cuprorivaite and liebauite are very rare. In the meantime liebauite has also been found in xenoliths of the Nickenicher Sattel (Osteifel) and at the Emmelberg (Westeifel) scoria cones.

The name is for Prof. Dr. Friedrich Liebau, Kiel, whose scientific work on silicate crystal chemistry has greatly enhanced our knowledge about this important class of minerals. Mineral and name have been approved prior to publication by the IMA commission on New Minerals and Mineral Names (#90−040). Type material has been deposited at the Mineralogisches Museum der Universität, Würzburg, Germany and at the Mineralogisches Museum der Universität, Kiel, Germany.

Chemistry and physical properties

The chemical analyses were carried out with a CAMECA SX50 microprobe (10 nA, 15 kV) using andradite as standard for calcium, metallic copper

for Cu, and orthoclase for Si since a preliminary energy dispersive scan had shown only copper, calcium, and silicon as main components. Two crystal grains were analyzed at three different spots each. Averaging of the six analyses resulted in 15.0(2) wt% CaO, 34.9(4) wt% CuO and 48.5(9) wt% SiO_2 with a total of 98.4 wt%. The empirical formula calculated on the basis of 26 oxygen atoms is $Ca_{2.99}Cu_{4.91}Si_{9.05}O_{26}$, giving an idealized chemical formula of $Ca_3Cu_5Si_9O_{26}$.

The mineral occurs as very small (< 0.03 mm) bluish-green transparent crystals with a vitreous lustre and a Mohs hardness between 5 and 6. Pleochroism was not observed. For the optical investigations a spindle stage with internal refractometer (Medenbach, 1980) was used. Because the theoretical mean refractive index as calculated from the Gladstone-Dale relationship (Gladstone and Dale, 1863; Larsen, 1921; Mandarino, 1976) is high (1.706), smithsonite ($n = 1.62 - 1.84$) was used as a refractometer crystal. The angle of the optical axes determined graphically from the recorded extinction curve according to the method of Joel (1963) is $2V_z = 72.8°$. The optical character of liebauite is positive with $\alpha = 1.722(1)$, $\beta = 1.723(1)$ and $\gamma = 1.734(1)$. The optical axis angle calculated from the main refractive indices differs with 33° distinctly from the value derived graphically. Bloss (1981), however, has pointed out that the equation used to calculate the angle of the optical axes can lead to large errors for cases of low birefringence as in liebauite where the birefringence is only 0.012. The compatibility value $|1 - K_p/K_c|$, which compares refractive indices, density, and chemical composition, is 0.032 and thus excellent (Mandarino, 1981).

For lack of material only a few crystal grains were available to record a powder pattern with a Debye-Scherrer camera (diameter 57.3 mm). The pattern is given in Table 1. One of the twenty observed reflections could definitely be identified as a cuprorivaite reflection (PDF # 12-512). Further superpositions of cuprorivaite and liebauite reflections are marked with asterisks.

Determination of the crystal structure

Peak-search and indexing routines on an automatic 4-circle X-ray diffractometer (Enraf-Nonius CAD-4, $MoK\alpha$-radiation, graphite monochromator) and subsequent precession photographs yielded a monoclinic cell, space group $C2/c$ (#15) with $a = 10.160(1)$, $b = 10.001(1)$, $c = 19.973(2)$ Å, $\beta = 91.56(2)°$, $V = 2028.7$ Å^3, $Z = 4$ and $d_{calc} = 3.62$ Mg/m^3. The lattice constants were refined from the settings of 25 high-angle reflections which had been centered on the diffractometer. The intensities of 3782 reflections up to $\sin \theta/\lambda = 0.60$ A^{-1} were collected in $\Omega/2\theta$ step scan mode with a scan width of $0.6 + 0.35 \tan\theta$. No intensity drop or change of crystal

Table 1. X-ray powder diffraction pattern of liebauite recorded with a Debye-Scherrer camera ($d = 57.3$ mm). Coincidences with cuprorivaite reflections are marked with asterisks.

d_o	I_o	hkl			d_c	I_c
7.69*	10					
7.13	60	1	1	0	7.126	44
6.70	70	1	1	$\bar{1}$	6.752	37
		1	1	1	6.671	26
5.82	10	1	1	$\bar{2}$	5.853	12
4.96	30	0	2	0	5.001	14
		0	0	4	4.991	6
		1	1	$\bar{3}$	4.911	12
4.56	30	2	0	$\bar{2}$	4.577	16
4.10	20	1	1	4	4.052	9
3.58	40	2	2	0	3.563	20
3.49	30	2	2	$\bar{1}$	3.519	1
		2	0	4	3.512	5
		1	1	$\bar{5}$	3.512	18
		1	1	5	3.456	16
3.33*	20	2	2	2	3.336	8
3.20*	40	3	1	0	3.207	24
3.12	90	1	3	$\bar{1}$	3.132	43
		1	3	1	3.124	48
3.00*	100	3	1	$\bar{2}$	3.030	25
		1	3	$\bar{2}$	3.027	9
		1	3	2	3.012	2
		1	1	6	2.993	91
2.94	10	2	2	$\bar{4}$	2.927	27
2.84	10	3	1	3	2.860	2
		1	3	$\bar{3}$	2.851	5
		2	0	$\bar{6}$	2.819	12
2.73	10	3	1	$\bar{4}$	2.730	17
2.66	10	1	1	$\bar{7}$	2.666	17
2.45	60	2	2	$\bar{6}$	2.455	66
2.41	70	2	2	6	2.409	100
1.78*	50	4	4	0	1.782	50

orientation was observed during data collection. Lorentz-polarisation and absorption effects were corrected. Averaging of symmetrically equivalent reflections gave a set of 1 785 unique and not systematically absent intensi-

Table 2. Fractional atomic coordinates and isotropic displacement parameters ($Å^2$).

Atom	x/a	y/b	z/c	B_{iso}
Cu(1)	0.2500	0.2500	0.5000	0.61(4)
Cu(2)	0.2312(2)	0.2581(2)	0.3391(1)	0.60(3)
Cu(3)	0.9704(2)	0.0105(2)	0.3284(1)	0.56(3)
Ca(1)	0.5000	0.2251(5)	0.2500	0.29(7)
Ca(2)	0.9725(3)	0.2641(3)	0.4297(1)	0.48(5)
Si(1)	0.9967(3)	0.7545(5)	0.4117(2)	0.42(7)
Si(2)	0.1987(4)	0.5451(5)	0.4066(2)	0.45(7)
Si(3)	0.2275(4)	0.5348(5)	0.6960(2)	0.56(7)
Si(4)	0.0000	0.7200(6)	0.7500	0.47(10)
Si(5)	0.2854(4)	0.5348(4)	0.5511(2)	0.25(6)
O(1)	0.0902(9)	0.6469(10)	0.3721(4)	0.85(20)
O(2)	0.9135(9)	0.8293(10)	0.3526(4)	0.49(18)
O(3)	0.9583(8)	0.8067(10)	0.6842(4)	0.24(17)
O(4)	0.9141(9)	0.6854(11)	0.4672(4)	0.75(19)
O(5)	0.1886(9)	0.3830(11)	0.7089(4)	0.55(19)
O(6)	0.1570(9)	0.3919(11)	0.3954(4)	0.65(19)
O(7)	0.3786(9)	0.5716(11)	0.7161(4)	0.66(18)
O(8)	0.1889(8)	0.5768(10)	0.4882(4)	0.24(18)
O(9)	0.1957(9)	0.5769(11)	0.6159(4)	0.51(18)
O(10)	0.1286(9)	0.6277(10)	0.7386(4)	0.59(18)
O(11)	0.3420(8)	0.3861(11)	0.5547(4)	0.38(18)
O(12)	0.5947(9)	0.3596(10)	0.4516(4)	0.70(20)
O(13)	0.1572(9)	0.0897(11)	0.1151(4)	0.90(20)

ties, 818 of which with $I > 3\sigma(I)$ were used in structure refinement. Atomic scattering factors and correction factors for anomalous dispersion were taken from International Tables for X-ray Crystallography Vol. IV (1974), computer programs used were SDP/VAX (Frenz, 1978), SHELX76 (Sheldrick, 1976), SADIAN86 (Baur, Wenninger and Roy, 1986), STRUPLO84 (Fischer, 1985) and a program system for crystal chemical classification of silicates (Goetzke et al., 1988).

The crystal structure was determined from Patterson and Fourier syntheses and refined with least-squares methods to a conventional residual $R = 0.046$ and $R_w = 0.044$ (86 variable parameters, isotropic displacement parameters). The R-value for all 1785 reflections was 0.124.[1] The refined atomic coordinates and isotropic displacement parameters are given in Table 2.
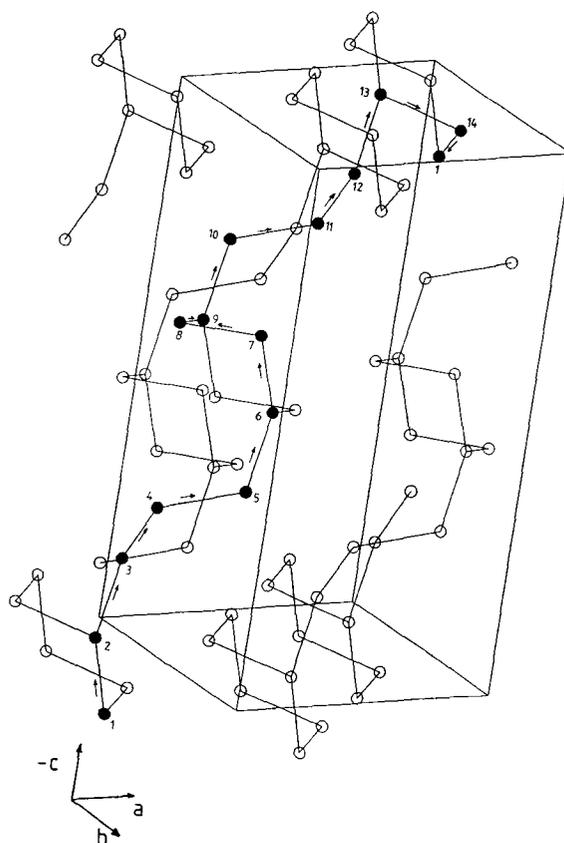
Fig. 1. The loop branched 14cr single chain of liebauite. Only the central silicon atoms of the tetrahedra are shown, neighbouring Si-atoms are connected.

Discussion

Apart from the tetragonal layer silicate cuprorivaite, $CaCuSi_4O_{10}$ (Mazzi and Pabst, 1962), liebauite is the second H_2O-free $Ca-Cu$ silicate found in nature. It is a loop branched single chain silicate with two loop branches within one chain period of 18 SiO_4 tetrahedra and a periodicity p of 14 according to Liebau (1985). As can be seen in Figure 1 the arrangement of the SiO_4 tetrahedra in the chain can clearly be described as 6-rings connected by three bridging tetrahedra. A schematic arrangement of the silicon and the bridging oxygen atoms is shown in Figure 2 and a projection of the crystal structure along [001] in polyhedral representation in Figure 3. The silicate chain shows an appreciable amount of shrinkage with a low
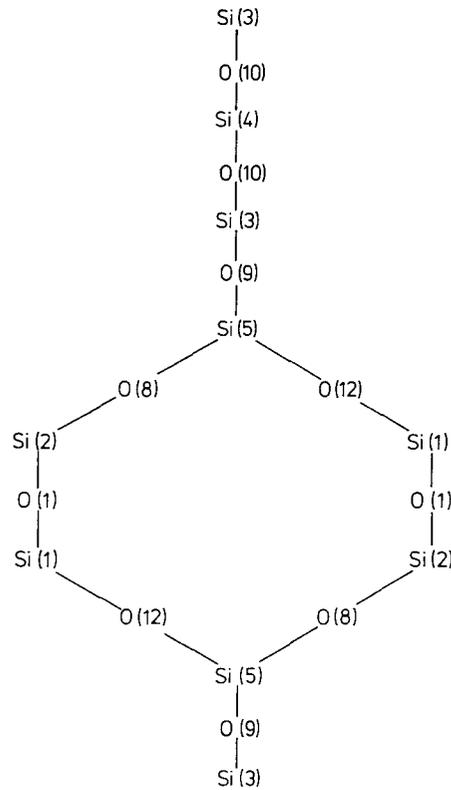
Fig. 2. Schematic arrangement of silicon atoms and bridging oxygen atoms of the silicate chain.

stretching factors f_s (Liebau and Pallas, 1981) of 0.599, the length of the chain period is 22.65 Å in the direction [10$\bar{1}$]. According to the classification of Liebau (1985), which depends on the arrangement of the SiO$_n$-polyhedra, the structural formula for the new mineral liebauite is Ca$_6$Cu$_{10}$ $\{$lB$,1^1_\infty\}[^{[4]}$Si$_{18}$O$_{52}]$.

Selected interatomic distances and angles are given in Tables 3 and 4. Individual Si—O distances vary between 1.569 and 1.677 Å with a mean distance of 1.624 Å, the variation of O—Si—O angles is 101.8 to 119.0°, Si—O—Si angles are between 125.8 and 155.5°. Bond strengths sums for the oxygen atoms (Table 5) calculated according to Brown and Wu (1976) and Brown (1981) vary between 1.82 and 2.15 v. u. which can be considered as normal.

Looking at such a complicated structure like that of liebauite one is inclined to wonder how nature is able to create crystals of such structural
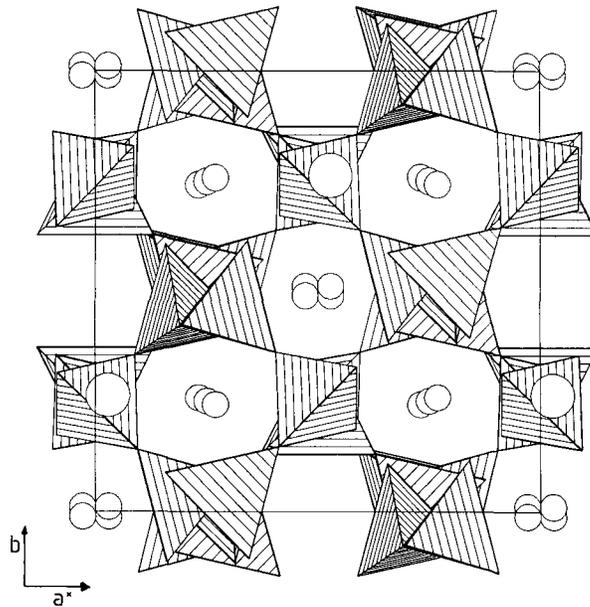
Fig. 3. Projection of the crystal structure of liebauite along [001].

Table 3. Cation-anion distances in liebauite (Å). Standard deviations are less than 0.01 Å

	Cu(1)	Cu(2)	Cu(3)	Ca(1)	Ca(2)	Si(1)	Si(2)	Si(3)	Si(4)	Si(5)
O(1)				2.698		1.651	1.639			
O(2)		1.996	1.966	2.481		1.617				
O(3)		2.072	1.985		2.502				1.621	
O(4)	1.920				2.386	1.569				
O(5)		1.902		2.366				1.592		
O(6)	2.677	1.916			2.385		1.604			
O(7)			1.973	2.463				1.619		
			2.542							
O(8)					2.838		1.666			1.628
O(9)					2.489			1.677		1.657
O(10)		2.511						1.626	1.621	
O(11)	1.966	2.687			2.424					1.595
O(12)					2.776	1.640				1.614
O(13)			1.913		2.348		1.601			

complexity and how these structures are stabilized. Essential information about the correlation between cation properties like electronegativity, valence and ionic radius and the shape of silicate chains or the stability of branches within the chain has been given by Liebau (1981, 1985).

Table 4. O — Si — O angles (°) and O — O-distances (Å) of the SiO_4 tetrahedra in liebauite.

Si	O	Si	O — Si — O-angle [°]	O — O-distance [Å]
O(4)	Si(1)	O(2)	116.2(5)	2.70
O(4)	Si(1)	O(12)	105.6(5)	2.56
O(4)	Si(1)	O(1)	112.2(6)	2.67
O(2)	Si(1)	O(12)	110.9(6)	2.68
O(2)	Si(1)	O(1)	104.4(5)	2.58
O(12)	Si(1)	O(1)	107.5(5)	2.65
O(13)	Si(2)	O(6)	117.9(6)	2.75
O(13)	Si(2)	O(1)	108.8(5)	2.64
O(13)	Si(2)	O(8)	106.9(5)	2.63
O(6)	Si(2)	O(1)	111.3(5)	2.68
O(6)	Si(2)	O(8)	107.2(5)	2.63
O(1)	Si(2)	O(8)	103.6(5)	2.60
O(5)	Si(3)	O(7)	114.5(6)	2.70
O(5)	Si(3)	O(10)	107.5(5)	2.59
O(5)	Si(3)	O(9)	110.6(5)	2.69
O(7)	Si(3)	O(10)	109.6(5)	2.65
O(7)	Si(3)	O(9)	109.7(5)	2.69
O(10)	Si(3)	O(9)	104.5(5)	2.61
O(3)	Si(4)	O(3)	115.3(6)	2.74
O(3)	Si(4)	O(10)	112.6(4)	2.70
O(3)	Si(4)	O(10)	103.0(4)	2.54
O(3)	Si(4)	O(10)	103.0(4)	2.54
O(3)	Si(4)	O(10)	112.6(4)	2.70
O(10)	Si(4)	O(10)	110.6(6)	2.66
O(11)	Si(5)	O(12)	109.9(5)	2.63
O(11)	Si(5)	O(8)	119.0(5)	2.78
O(11)	Si(5)	O(9)	114.0(5)	2.73
O(12)	Si(5)	O(8)	104.2(5)	2.56
O(12)	Si(5)	O(9)	106.9(5)	2.63
O(8)	Si(5)	O(9)	101.8(5)	2.55

Of some influence is the high electronegativity of the Cu^{2+}-cation. Strongly electronegative cations do not tend to give up all valence electrons to the tetrahedral anions which would increase the negative charge per tetrahedron. The resulting stronger repulsion between neighbouring tetrahedra would then lead to a larger stretching factor. The same is true for a loop branch as compared to an open branch. Loop branches increase the Si : O-ratio, which also results in a lower negative charge per tetrahedron.

An additional factor explaining the low stretching factor of the liebauite chain is the relative high mean valence of the non-tetrahedral cations Cu^{2+} and Ca^{2+}, which has to be compensated by a larger number of non-bridging oxygen atoms. Purely geometrical considerations show, that a low ratio of

Table 5. Bond strengths sums for the oxygen atoms calculated after Brown and Wu (1976) and Brown (1981).

	Cu(1)	Cu(2)	Cu(3)	Ca(1)	Ca(2)	Si(1)	Si(2)	Si(3)	Si(4)	Si(5)	Σ
O(1)				0.15	0.94	0.98					2.07
O(2)		0.41	0.44	0.24		1.04					2.13
O(3)		0.32	0.42		0.23				1.03		2.00
O(4)	0.51				0.30	1.18					1.99
O(5)		0.54		0.31				1.11			1.96
O(6)	0.07	0.52			0.30		1.07				1.96
O(7)			0.44 0.10	0.25				1.03			1.82
O(8)					0.12		0.90			1.01	2.03
O(9)					0.24			0.88		0.93	2.05
O(10)		0.10						1.01	1.03		2.14
O(11)	0.45	0.07			0.28					1.10	1.90
O(12)					0.13	0.97				1.05	2.15
O(13)			0.52		0.33		1.08				1.93
											26.13

non-tetrahedral cations versus non-bridging oxygen atoms causes a strongly folded chain, since all non-bridging oxygen atoms of the tetrahedral anions also participate in the coordination sphere of the cations.

Finally, we must regard the influence of the 'soft' cation Cu^{2+} on the stability of a loop branched single chain silicate. 'Soft' cations decrease structural stress, because they can adjust to coordination polyhedra of variable number and size and occupy the positions offered by the structure.

The coordination of oxygen atoms around copper in liebauite is [4 + 2] for Cu(1) and Cu(2) and [4 + 1] in the case of Cu(3). Such coordination polyhedra, probably caused by Jahn-Teller distortion, are often observed for divalent copper (Zemann, 1972). The arrangement of the four closer oxygen atoms is almost planar with values of 360, 360.5 and 358.7° for the sums of the four $O-Cu-O$ angles around Cu(1), Cu(2) and Cu(3), respectively. The average $Cu-O$ distances in the planes are 1.943, 1.972 and 1.959 Å. The CuO_4 planes of the three crystallographically different copper positions are not parallel but inclined to each other, an arrangement which usually inhibits a pleochroic effect (Zemann, 1961). Consequently pleochroism has not been observed in liebauite.

Figure 4 shows the arrangement of the copper-oxygen polyhedra in a projection along [001]. Distorted $Cu(1)O_6$ octahedra with site symmetry $\bar{1}$ alternating at 1/4 1/4 1/2 and at 1/4 3/4 0 link two distorted $Cu(2)O_6$ octahedra each (at $z/c = 0.34$ and 0.66 and alternatively at $z/c = 0.84$ and 1.16) via common edges $O(6)-O(11)$ to form columns of three octahedra along [001]. One unit cell contains four of these columns which are connected via common corners by the $Cu(3)O_5$ pyramids in approximately 0 0 z/c
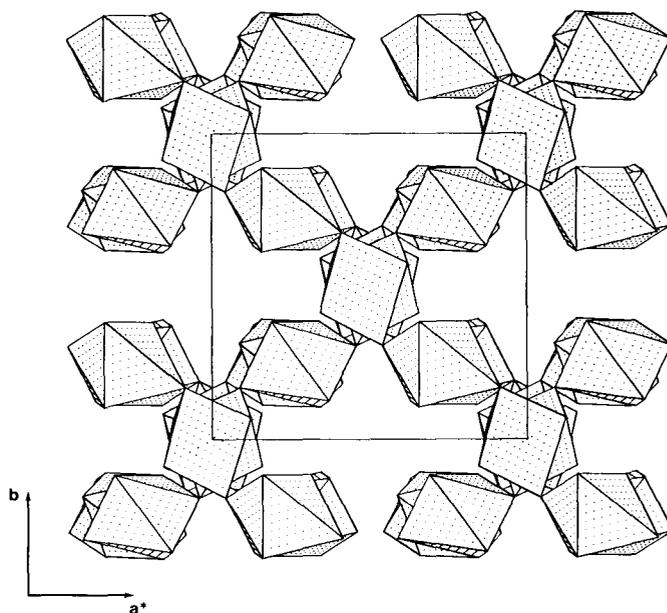
Fig. 4. Arrangement of oxygen coordination polyhedra around copper in liebauite. Projection along [001].

and $1/2$ $1/2$ z/c with $z/c = 0.17$, 0.33, 0.67 and 0.83 to form infinite chains in directions [110] and [1$\bar{1}$0]. The chains intersect each other at the $Cu(3)O_5$ polyhedra, each two of which (at $z/c = 0.17$ and 0.33 and 0.67 and 0.83, respectively) share one edge.

There are no close structural relations between other calcium copper or copper silicates and liebauite. While cuprorivaite, $CaCuSi_4O_{10}$, is a layer silicate with a square planar coordination of oxygen atoms around copper, shattuckite, $Cu_5(SiO_3)_4(OH)_2$ (Evans and Mrose, 1977) is an unbranched 2er single chain silicate with a pyroxene-type $(SiO_3)_n$ chain and the highest possible stretching factor $f_s = 1$, despite of the relatively high electronegativity of copper. It has been shown by Liebau, however, that the short periodicity of $p = 2$ is necessarily connected with a high stretching factor. Structurally and in its occurrence closely related to shattuckite is plancheite, $Cu_8[(Si_4O_{11})_2/(OH)_4] \cdot xH_2O$ (Evans and Mrose, 1977).

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