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Three Modifications of $BaCu(SeO_3)_2$ and the Compound $SrCu(SeO_3)_2$: Preparation and Crystal Structure Determination*

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The crystal structures of four hydrothermally synthesized alkaline earth–copper–selenites were determined: $BaCu(SeO_3)_2$-I [$a = 5.247(1)$, $b = 13.353(2)$, $c = 8.981(1)$ Å, space group $Pnm2_1$, $Z = 4$, $R_w = 0.024$ for 1270 reflections], $BaCu(SeO_3)_2$-II [$a = 5.256(1)$, $b = 13.231(2)$, $c = 8.933(1)$ Å, $\beta = 90.19(1)°$, space group $P2_1/c$, $Z = 4$, $R_w = 0.046$ for 2238 reflections], $BaCu(SeO_3)_2$-III [$a = 8.031(1)$, $b = 5.185(1)$, $c = 15.823(2)$ Å, $\beta = 90.83(1)°$, space group $C2/c$, $Z = 4$, $R_w = 0.038$ for 1866 reflections], and $SrCu(SeO_3)_2$ [$a = 7.929(1)$, $b = 5.132(1)$, $c = 14.997(2)$ Å, $\beta = 90.53(1)°$, space group $C2/c$, $Z = 4$, $R_w = 0.028$ for 1414 reflections; isotypic with $BaCu(SeO_3)_2$-III].

$BaCu(SeO_3)_2$-I and -II contain $Cu(SeO_3)_2$ sheets lying parallel to (100) formed by CuO_4 "squares" and selenite groups. These sheets are topologically different: in $BaCu(SeO_3)_2$-I they are formed by the connection of $Cu_2(SeO_3)$ and $Cu_6(SeO_3)_4$ rings while in $BaCu(SeO_3)_2$-II they are formed by $Cu_2(SeO_3)_2$ and $Cu_6(SeO_3)_6$ rings. The $Cu(SeO_3)_2$ sheets are rugged in $BaCu(SeO_3)_2$-I and they are slightly waved in $BaCu(SeO_3)_2$-II. In both compounds they are connected to each other by a fifth Cu–O bond and by the Ba atoms. In $BaCu(SeO_3)_2$-III and in its isotypic Sr analog the CuO_4 "squares" and the selenite groups form parallel chains [010], which are connected by the alkaline earth atoms.

Introduction

Although the number of known crystal structures of oxygen-bearing copper(II) compounds is very large, no alkaline earth–copper(II)–selenite was investigated until now. The structures of the following copper selenites are described in the literature: $Cu(SeO_3)$-I (*1*), $CuSe_2O_5$ (*2*), $Cu(SeO_3)_2 \cdot 2H_2O$ (chalcomenite) (*3*), $Cu_4(UO_2)(OH)_6(SeO_3)_2$ (derriksite) (*4*), $Pb_2Cu_5(SeO_3)_6(UO_2)_2(OH)_6 \cdot 2H_2O$ (demesmaekerite) (*5*), and $Cu_5Se_2O_8Cl_2$ (*6*). The present structure analyses are part of a systematic investigation of copper(II)–selenites grown under hydrothermal conditions. In connection with this topic, the structures of the following compounds were solved: $Cu(SeO_3)$-II, -III, -IV (*7*), $Cu_2O(SeO_3)$-I, -II (*8*), $Cu_4O(SeO_3)_3$-I, -II (*8*), $Cu(SeO_2OH)_2$ (*9*), $PbCu_2(SeO_3)_3$ (*10*), $PbCu_3(OH)(NO_3)(SeO_3)_3 \cdot \frac{1}{2}H_2O$ (*11*), $Pb_2Cu_3O_2(NO_3)_2(SeO_3)_2$ (*11*), $Pb_2Cu_2(OH)_4(SeO_3)(SeO_4)$ (schmiederite) (*12*), $Sr_2Cu(SeO_3)_3$ (*13*), and $Sr_2Cu(SeO_3)_2(SeO_2OH)_2$ (*13*), besides $BaCu(SeO_3)_2$-I, -II, -III, and $SrCu(SeO_3)_2$ (this work).

Experimental

Crystals for structure determination were prepared under hydrothermal conditions in

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a steel vessel lined with Teflon (~6 ml capacity). Two grams of a molar mixture of CuO, SeO_2, and hydroxides or carbonates of Sr and Ba, respectively, were inserted; the vessels were filled up with H_2O to about 80 vol%. The closed vessels were heated to 503(10) K for 5 days and afterward cooled to room temperature. The following phases were observed: in Ba-bearing runs the three modifications of $BaCu(SeO_3)_2$, in Sr-bearing runs $SrCu(SeO_3)_2$, $Sr_2Cu(SeO_3)_3$, and $Sr_2Cu(SeO_3)_2(SeO_2OH)_2$. In addition crystals of $Cu(SeO_3)$-II, -III, and -IV, $Cu(SeO_3) \cdot 2H_2O$ (chalcomenite), $Cu_2O(SeO_3)$-I and -II, and $Cu_4O(SeO_3)_3$-I and -II were obtained in changing amounts. The crystals have maximum sizes of 0.4 mm.

The crystal data and relevant data concerning the measurement of the X-ray intensities are summarized in Table I. An empirical absorption correction according to several ψ scans as well as corrections for Lorentz and polarization effects were applied. The Ba and Sr atoms and parts of the Se and Cu atoms were located by direct method strategies. Subsequent Fourier and difference Fourier summations revealed the positions of all the other atoms. Complex neutral atomic scattering functions were used (*14*). Correction for isotropic secondary extinction (*15*) was applied during the last stage of refinement. All calculations were performed with the program system STRUCSY (Stoe & Cie, Darmstadt, FRG) on an ECLIPSE S140 (Data General). Table II gives the final obtained structure parameters.

The refinement of the acentric structure of $BaCu(SeO_3)_2$-I with an atomic parameter set $(\bar{x}\ \bar{y}\ \bar{z})$ gave $R_w = 0.028$ as compared with $R_w = 0.024$ for the atomic coordinates $(x\ y\ z)$. This indicates that the configuration of the investigated crystal accords with the data given in Table II.

Discussion

Within the three polymorphs of $BaCu(SeO_3)_2$ the Ba–O bonds range from 2.74 to 3.35 Å; up to 4.00 Å no further O atom

TABLE I

CRYSTAL DATA, X-RAY DATA COLLECTION, AND RESULTS OF STRUCTURE REFINEMENT (ESD'S IN PARENTHESES)

	$BaCu(SeO_3)_2$-I	$BaCu(SeO_3)_2$-II	$BaCu(SeO_3)_2$-III	$SrCu(SeO_3)_2$
a [Å]	5.247(1)	5.256(1)	8.031(1)	7.929(1)
b [Å]	13.353(2)	13.231(2)	5.185(1)	5.132(1)
c [Å]	8.981(1)	8.933(1)	15.823(2)	14.997(2)
β [Å]	—	90.19(1)	90.83(1)	90.53(1)
V [Å^3]	629.2	621.2	658.8	610.2
Space group	$Pnm2_1$	$P2_1/c$	$C2/c$	$C2/c$
Z	4	4	4	4
μ(Mo$K\alpha$) [cm^{-1}]	204	207	195	236
ρ_{calc} [g cm^{-3}]	4.80	4.86	4.59	4.41
Color	Light green	Light green	Dark blue	Dark blue
Crystal dimensions [mm^3]	0.04 × 0.07 × 0.18	0.03 × 0.05 × 0.26	0.16 × 0.20 × 0.28	0.06 × 0.10 × 0.16
Diffractometer	Four-circle diffractometer AED2 (Stoe & Cie, Darmstadt, FRG)			
Radiation; reflection measurement	Mo$K\alpha$ (graphite monochromatized); scan mode $2\theta/\omega$; step width 0.03°, measuring time 0.5 to 1.5 sec/step			
Min. step No. + $(\alpha_1\alpha_2)$ dispersion	45	45	47	45
2θ max [°]	70	70	80	75
Measured reflections	3185	3853	4874	3260
Unique data	1513	2735	2052	1601
Data with $F_o > 3\sigma(F_o)$	1270	2238	1866	1414
Variables	97	92	49	49
R	0.032	0.055	0.040	0.035
R_w, $w = [\sigma(F_o)]^{-2}$	0.024	0.046	0.038	0.028

TABLE II

FRACTIONAL ATOMIC PARAMETERS AND ANISOTROPIC TEMPERATURE PARAMETERS
(ATF = $\exp[-2\pi^2 \Sigma_{i=1}^{3} \Sigma_{j=1}^{3}, U_{ij}h_ih_ja_i^*a_j^*]$)

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{iso}
$BaCu(SeO_3)_2$-I (space group $Pnm2_1$)										
Ba	−0.0016(1)	0.20084(3)	$\frac{1}{4}$*	0.0148(2)	0.0143(2)	0.0143(2)	0.0001(2)	−0.0015(2)	−0.0011(2)	0.0145
Cu	0.4572(2)	0.13138(7)	0.5463(1)	0.0171(5)	0.0088(4)	0.0105(4)	0.0015(3)	−0.0008(4)	−0.0006(3)	0.0121
Se(1)	0.5231(3)	0	0.2299(1)	0.0202(6)	0.0099(4)	0.0106(5)	0	0.0008(5)	0	0.0136
Se(2)	0.9170(2)	0	0.6613(2)	0.0136(5)	0.0122(4)	0.0199(5)	0	−0.0024(4)	0	0.0152
Se(3)	0.5058(2)	0.14297(6)	0.9171(1)	0.0153(3)	0.0093(3)	0.0119(3)	0.0005(3)	0.0002(3)	0.0011(2)	0.0122
O(11)	0.458(1)	0.1035(4)	0.3345(7)	0.033(4)	0.013(2)	0.012(2)	0.009(3)	−0.002(3)	−0.001(2)	0.019
O(12)	0.840(2)	0	0.2207(13)	0.025(5)	0.022(4)	0.047(7)	0	0.015(5)	0	0.031
O(21)	1.027(1)	0.1022(4)	0.5728(9)	0.024(3)	0.010(2)	0.043(4)	−0.010(3)	0.002(3)	0.002(3)	0.026
O(22)	0.596(2)	0	0.6006(11)	0.018(4)	0.006(3)	0.028(4)	0	−0.003(4)	0	0.017
O(31)	0.527(1)	0.1874(4)	0.7413(8)	0.028(3)	0.020(3)	0.011(2)	0.000(3)	0.000(3)	−0.002(2)	0.020
O(32)	0.689(1)	0.2326(4)	1.0029(7)	0.017(3)	0.015(3)	0.015(2)	0.002(2)	−0.006(2)	0.005(2)	0.016
O(33)	0.211(1)	0.1768(6)	0.9665(8)	0.009(3)	0.036(4)	0.024(3)	0.001(3)	0.005(2)	0.004(3)	0.023
$BaCu(SeO_3)_2$-II (space group $P2_1/c$)										
Ba	0.7321(1)	0.29888(5)	0.19285(6)	0.0159(2)	0.0125(3)	0.0146(2)	0.0001(2)	−0.0013(2)	0.0001(2)	0.0143
Cu	0.2743(2)	0.1325(1)	0.4006(1)	0.0171(5)	0.0120(6)	0.0199(4)	−0.0019(5)	0.0005(3)	0.0006(4)	0.0136
Se(1)	0.8104(2)	0.00836(9)	0.2901(1)	0.0157(4)	0.0115(5)	0.0152(4)	−0.0003(4)	0.0004(3)	0.0014(4)	0.0142
Se(2)	0.2382(2)	0.13778(9)	0.0353(1)	0.0177(4)	0.0117(5)	0.0124(3)	−0.0008(4)	−0.0029(3)	0.0001(4)	0.0139
O(11)	0.708(1)	−0.0934(6)	0.3887(7)	0.036(4)	0.013(4)	0.015(3)	−0.001(4)	0.009(3)	0.010(3)	0.022
O(12)	1.133(1)	0.0034(6)	0.3282(8)	0.016(3)	0.013(4)	0.027(3)	0.000(3)	−0.004(2)	−0.006(3)	0.018
O(13)	0.715(2)	0.1136(6)	0.3790(8)	0.035(4)	0.012(4)	0.019(3)	−0.003(3)	0.002(3)	−0.007(3)	0.022
O(21)	0.223(1)	0.1942(6)	0.2068(7)	0.026(3)	0.019(4)	0.011(3)	0.003(3)	0.001(2)	0.002(3)	0.019
O(22)	0.423(1)	0.2279(6)	−0.0481(7)	0.022(3)	0.018(4)	0.018(3)	−0.003(3)	0.008(2)	−0.004(3)	0.020
O(23)	−0.055(1)	0.1580(7)	−0.0309(8)	0.018(3)	0.036(6)	0.030(4)	0.005(4)	−0.007(3)	−0.004(4)	0.028
$BaCu(SeO_3)_2$-III (space group $C2/c$)										
Ba	0	−0.01597(4)	$\frac{1}{4}$	0.0104(1)	0.0162(1)	0.0125(1)	0	0.0026(1)	0	0.0130
Cu	0	0	0	0.0150(2)	0.0095(2)	0.0131(2)	−0.0010(1)	0.0018(2)	0.0005(1)	0.0125
Se	0.36468(4)	0.00317(4)	0.09213(2)	0.0112(1)	0.0125(1)	0.0127(1)	−0.0004(1)	0.0008(1)	−0.0004(1)	0.0121
O(1)	0.3218(3)	0.0348(5)	0.1947(2)	0.016(1)	0.033(1)	0.017(1)	−0.006(1)	0.007(1)	−0.005(1)	0.022
O(2)	0.5231(3)	0.2210(4)	0.0820(2)	0.017(1)	0.016(1)	0.022(1)	−0.005(1)	−0.001(1)	0.005(1)	0.018
O(3)	0.4727(4)	−0.2787(4)	0.0959(2)	0.035(2)	0.013(1)	0.016(1)	0.007(1)	−0.002(1)	−0.001(1)	0.022
$SrCu(SeO_3)_2$ (space group $C2/c$)										
Sr	0	−0.04691(8)	$\frac{1}{4}$	0.0116(2)	0.0173(2)	0.0115(2)	0	0.0019(1)	0	0.0135
Cu	0	0	0	0.0152(2)	0.0114(2)	0.0119(2)	−0.0008(2)	0.0019(2)	0.0003(1)	0.0128
Se	0.35603(4)	0.00199(5)	0.09444(2)	0.0112(1)	0.0130(1)	0.0121(1)	0.0000(1)	0.0005(1)	−0.0001(1)	0.0121
O(1)	0.3065(3)	0.0587(5)	0.2002(2)	0.018(1)	0.025(1)	0.016(1)	−0.005(1)	0.006(1)	−0.005(1)	0.020
O(2)	0.5256(4)	0.2079(4)	0.0826(2)	0.018(1)	0.016(1)	0.017(1)	−0.004(1)	−0.001(1)	0.004(1)	0.017
O(3)	0.4552(4)	−0.2922(4)	0.1041(2)	0.025(1)	0.015(1)	0.015(1)	0.004(1)	0.001(1)	0.001(1)	0.018

* Fixes the origin of the unit cell.

occurs. As can be seen from Table III the detailed coordinations are different. In $BaCu(SeO_3)_2$-I the 11 individual Ba–O distances are approximately statistically distributed between 2.77 and 3.21 Å. In $BaCu(SeO_3)_2$-II there is a gap of 0.320 Å between the 10th and the 11th Ba–O bond length, thus the coordination number [10 + 1] seems to be appropriate. In $BaCu(SeO_3)_2$-III a gap of 0.312 Å indicates [8 + 2] coordination for the Ba atom. The definitely smaller coordination number and the somewhat shorter Ba–O bond length in $BaCu(SeO_3)_2$-III as compared with $BaCu(SeO_3)_2$-I and -II may be taken as arguments that only for the former structure type the isotypic Sr compound could be synthesized. The eight shortest Sr–O bonds vary from 2.57 to 2.82 Å and the gap to the two next nearest O atoms is already 0.725 Å.

All the Cu atoms in the four title compounds have four nearest O atom neighbors

TABLE III

The Coordination of the Alkaline Earth Atoms (Ba–O, Resp. Sr–O Bonds up to 4.00 Å Are Given, ESD's in Parentheses)

$BaCu(SeO_3)_2$-I (space group *Pnm*2_1)	$BaCu(SeO_3)_2$-II (space group *P*2_1/*c*)
Ba–O(33) = 2.767(7)	Ba–O(23) = 2.765(7)
Ba–O(32) = 2.782(5)	Ba–O(12) = 2.803(8)
Ba–O(33′) = 2.799(6)	Ba–O(11) = 2.810(7)
Ba–O(12) = 2.820(3)	Ba–O(22) = 2.852(6)
Ba–O(11) = 2.844(6)	Ba–O(22′) = 2.855(6)
Ba–O(31) = 2.903(6)	Ba–O(21) = 2.932(7)
Ba–O(32) = 2.938(5)	Ba–O(23′) = 2.956(8)
Ba–O(21) = 3.077(6)	Ba–O(13) = 2.964(7)
Ba–O(31′) = 3.137(6)	Ba–O(21′) = 3.015(7)
Ba–O(21′) = 3.187(7)	Ba–O(13′) = 3.034(7)
Ba–O(11′) = 3.208(6)	Ba–O(11′) = 3.354(7)
$BaCu(SeO_3)_2$-III (space group *C*2/*c*)	**$SrCu(SeO_3)_2$ (space group *C*2/*c*)**
Ba–O(3) = 2.737(2) 2*x*	Sr–O(3) = 2.570(2) 2*x*
Ba–O(1) = 2.753(2) 2*x*	Sr–O(1) = 2.606(2) 2*x*
Ba–O(1′) = 2.864(2) 2*x*	Sr–O(1′) = 2.643(2) 2*x*
Ba–O(2) = 2.995(2) 2*x*	Sr–O(2) = 2.817(2) 2*x*
Ba–O(1″) = 3.307(2) 2*x*	Sr–O(1″) = 3.542(3) 2*x*

in an only slightly distorted "square planar" arrangement (for the detailed coordination figures see Table IV). In both $BaCu(SeO_3)_2$-I and -II one additional O atom completes the coordination figure to a tetragonal pyramid; next O atoms have Cu–O > 2.90 Å and are excluded from discussion of coordination. The mean Cu–O distances within the CuO_4 "squares" are longer for the [4 + 1]-coordinated Cu atoms [1.962 Å: $BaCu(SeO_3)_2$-I and 1.978 Å: $BaCu(SeO_3)_2$-II] than those for the [4]-coordinated Cu atoms [1.934 Å: $BaCu(SeO_3)_2$-III and 1.941 Å: $SrCu(SeO_3)_2$]. In $BaCu(SeO_3)_2$-III and $SrCu(SeO_3)_2$ the CuO_4 "squares" are exactly planar due to their site symmetry $\bar{1}$; in $BaCu(SeO_3)_2$-I and -II the Cu atoms are slightly shifted out of the least-squares planes defined by the four nearest O atom neighbors toward the fifth O atom. Similar coordination figures were described in many inorganic crystal structures for Cu(II) atoms (*16–19*).

As can be seen from Table V all but one

TABLE IV

The Coordination of the Cu Atoms (Cu–O Distances up to 2.90 Å Are Given; ESD's in Parentheses)

$BaCu(SeO_3)_2$-I (space group *Pnm*2_1)

Cu	O(11)	O(31)	O(22)	O(32)	O(21)
O(11)	*1.938(6)*	3.838(9)	2.853(10)	2.770(8)^a	3.117(10)
O(31)	163.6(3)	*1.939(6)*	2.826(7)	2.649(9)^a	3.239(10)
O(22)	94.1(3)	92.9(3)	*1.961(4)*	3.969(7)	3.293(11)
O(32)	89.1(3)	84.2(3)	176.8(3)	*2.010(5)*	2.736(9)^a
O(21)	94.1(3)	99.1(3)	100.8(3)	78.4(2)	*2.306(7)*

$BaCu(SeO_3)_2$-II (space group *C*2/*c*)

Cu	O(3)	O(3′)	O(2)	O(2′)
O(3)	*1.918(2)*	3.836(4)	2.635(3)^a	2.832(3)
O(3′)	180.0	*1.918(2)*	2.832(3)	2.635(3)^a
O(2)	85.9(1)	94.1(1)	*1.950(2)*	3.901(5)
O(2′)	94.1(1)	85.9(1)	180.0	*1.950(2)*

$BaCu(SeO_3)_2$-II (space group *P*2_1/*c*)

Cu	O(21)	O(11)	O(12)	O(22)	O(13)
O(21)	*1.931(6)*	3.867(9)	2.788(11)	2.634(9)^a	3.188(10)
O(11)	168.9(3)	*1.954(6)*	2.915(10)	2.845(11)^a	3.057(10)
O(12)	91.2(3)	95.9(3)	*1.970(7)*	4.020(11)	3.416(10)
O(22)	82.7(3)	90.4(3)	173.7(3)	*2.056(8)*	2.682(11)^a
O(13)	96.1(3)	90.3(3)	104.6(3)	74.9(3)	*2.339(7)*

$SrCu(SeO_3)_2$ (space group *C*2/*c*)

Cu	O(3)	O(3′)	O(2)	O(2′)
O(3)	*1.927(2)*	3.854(5)	2.646(3)^a	2.840(3)
O(3′)	180.0	*1.927(2)*	2.840(3)	2.646(3)^a
O(2)	86.0(1)	94.0(1)	*1.955(2)*	3.909(4)
O(2′)	94.0(1)	86.0(1)	180.0	*1.955(2)*

[a] Common O–O edge with the coordination polyhedron of the Ba (resp. Sr) atom.

TABLE V

THE COORDINATION OF THE Se ATOMS (ESD'S IN PARENTHESES)

$BaCu(SeO_3)_2$-I (space group *Pnm*2_1)

Se(1)	O(12)	O(11)	O(11′)
O(12)	*1.667(10)*	2.640(11)[a]	2.640(11)[a]
O(11)	103.1(3)	*1.706(5)*	2.765(10)
O(11′)	103.1(3)	108.3(4)	1.706(5)
Se(2)	O(21)	O(21′)	O(22)
O(21)	*1.681(6)*	2.729(11)	2.652(10)
O(21′)	108.6(5)	*1.681(6)*	2.652(10)
O(22)	100.3(3)	100.3(3)	*1.772(8)*
Se(3)	O(33)	O(31)	O(32)
O(33)	*1.671(6)*	2.620(10)[a]	2.637(8)
O(31)	102.4(3)	*1.691(6)*	2.570(9)[a]
O(32)	102.2(3)	97.9(3)	*1.718(5)*

$SrCu(SeO_3)_2$ (space group *C*2/*c*)

Se	O(1)	O(3)	O(2)
O(1)	*1.663(2)*	2.596(4)[a]	2.601(4)[a]
O(3)	100.7(1)	*1.708(2)*	2.647(3)
O(2)	100.5(1)	101.1(2)	*1.720(2)*

$BaCu(SeO_3)_2$-II (space group *P*2_1/*c*)

Se(1)	O(13)	O(11)	O(12)
O(13)	*1.680(8)*	2.739(12)	2.678(11)
O(11)	108.4(4)	*1.698(7)*	2.635(10)[a]
O(12)	103.4(4)	100.4(4)	*1.731(6)*
Se(2)	O(23)	O(21)	O(22)
O(23)	*1.672(7)*	2.619(10)[a]	2.682(10)
O(21)	101.7(4)	*1.706(6)*	2.550(9)[a]
O(22)	105.0(4)	96.6(4)	*1.710(7)*

$BaCu(SeO_3)_2$-III (space group *C*2/*c*)

Se	O(1)	O(3)	O(2)
O(1)	*1.672(2)*	2.570(4)[a]	2.609(4)[a]
O(3)	99.3(1)	*1.700(2)*	2.632(3)
O(2)	101.0(1)	101.0(1)	*1.711(2)*

[a] Common O–O edge with the coordination polyhedron around the Ba (resp. Sr) atoms.

of the individual Se–O bond lengths range from 1.663 to 1.731 Å; the exception is Se(2)–O(22) in $BaCu(SeO_3)_2$-I with 1.772 Å. This O(22) atom is the only oxygen atom within the four title compounds which belongs simultaneously to two CuO_4 "squares." The average Se–O bond length for the Se(2)O_3 group in $BaCu(SeO_3)_2$-I is 1.711 Å and is definitely larger than all the others, which range from 1.693 to 1.703 Å. The O–O edges of the selenite groups range from 2.550 to 2.640 Å when they are common edges with any coordination polyhedron around Sr or Ba atoms, and from 2.632 to 2.765 Å in all the other cases. These lengths of the O–O edges correspond to the O–Se–O angles varying for the former from 96.6 to 103.1° and for the latter from 100.3 to 108.6°. Similar dimensions of selenite groups were found in all copper selenites (*1–13*).

The comparison of $BaCu(SeO_3)_2$-I (Fig. 1) and -II (Fig. 2) from a topological point of view is of special interest. Both these compounds contain $Cu(SeO_3)_2$ sheets formed by the connection of CuO_4 "squares" and selenite groups. The sheets are arranged parallel to (100). In [100] they are connected by the fifth Cu–O bond and by the Ba atoms. Although the lattice parameters for these two compounds differ by less than 1%, the interconnection of the coordination polyhedra is different: in $BaCu(SeO_3)_2$-I each two CuO_4 "squares" share a common O–O corner building formal "Cu_2O_7 units"; in Ba $Cu(SeO_3)_2$-II the CuO_4 "squares" are isolated. Considering the connection of the CuO_4 "squares" by the selenite groups in

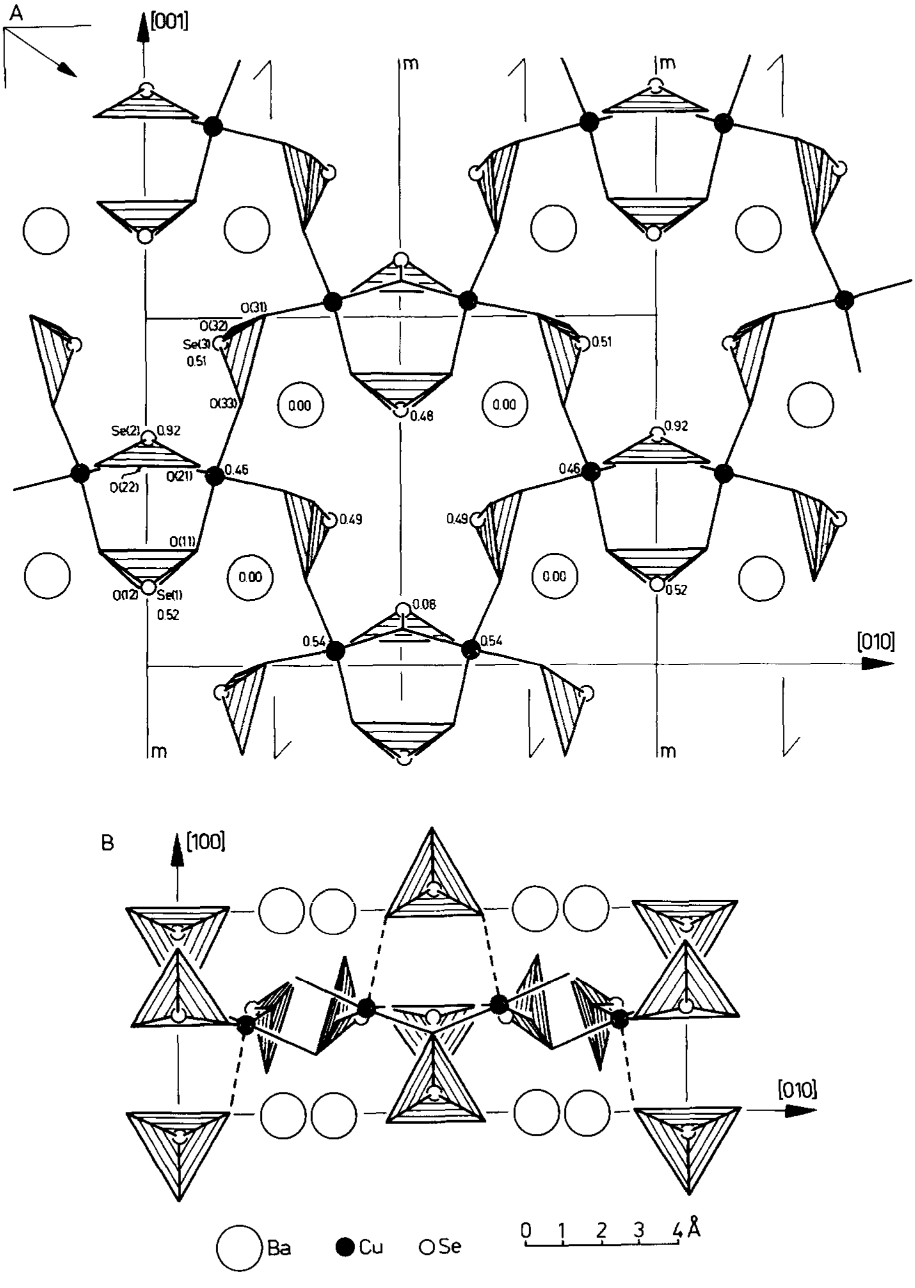

FIG. 1. The crystal structure of $BaCu(SeO_3)_2$-I in a projection (A) parallel [100] and (B) parallel [001]. Fractional atomic coordinates x/a and symmetry elements are indicated.

both these compounds the $Cu(SeO_3)_2$ sheets consist of two kinds of rings containing two and six Cu atoms, respectively. Because the CuO_4 "squares" are connected to each other only in $BaCu(SeO_3)_2$-II, the number of selenite groups within these rings varies: While $BaCu(SeO_3)_2$-I forms $Cu_2(SeO_3)$ and $Cu_6(SeO_3)_4$ rings with symmetry *m*, con-

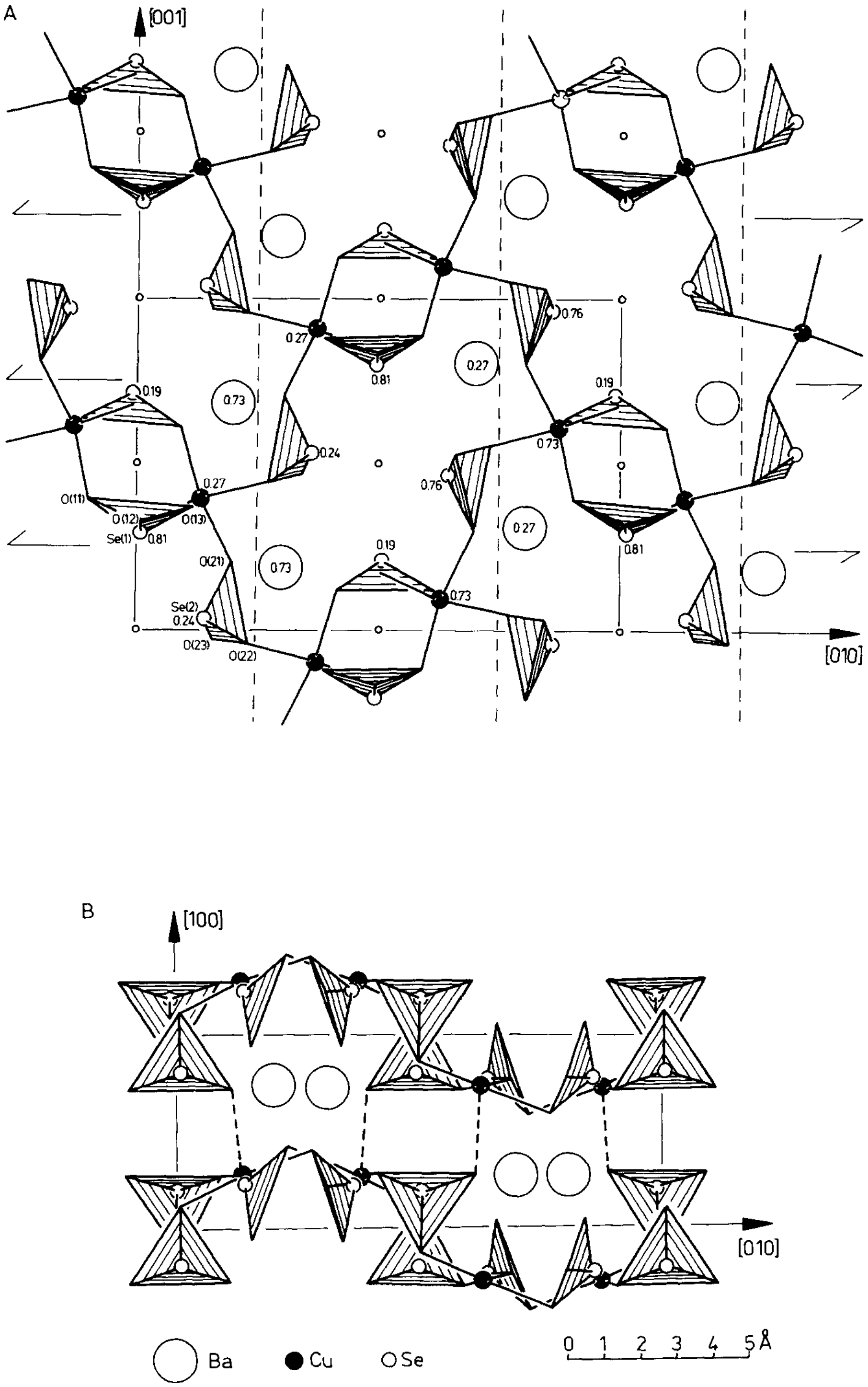

FIG. 2. The crystal structure of $BaCu(SeO_3)_2$-II in a projection (A) parallel [100] and (B) parallel [001]. Fractional atomic coordinates x/a and symmetry elements are indicated.

trary $BaCu(SeO_3)_2$-II forms $Cu_2(SeO_3)_2$ and $Cu_6(SeO_3)_6$ rings with symmetry $\bar{1}$.

In $BaCu(SeO_3)_2$-I all the Cu atoms are located at $x/a \sim \frac{1}{2}$ and the Ba atoms at $x/a \sim 0.0$; in $BaCu(SeO_3)_2$-II each half of the Cu and Ba atoms is located at $x/a \sim \frac{1}{4}$ and $\frac{3}{4}$ (see Figs. 1B and 2B). This results in two kinds of bending of the $Cu(SeO_3)_2$ sheets: In $BaCu(SeO_3)_2$-I the total thickness of the sheets is 5.53 Å (about 0.28 Å larger than the lattice parameter *a*). These sheets are rugged, and the $Se(2)O_3$ groups alternately point to opposite neighboring sheets. In $BaCu(SeO_3)_2$-II the thickness in only 4.45 Å (about 0.81 Å smaller than the lattice parameter *a*). These sheets are waved. In both these compounds the remaining holes house the Ba atoms.

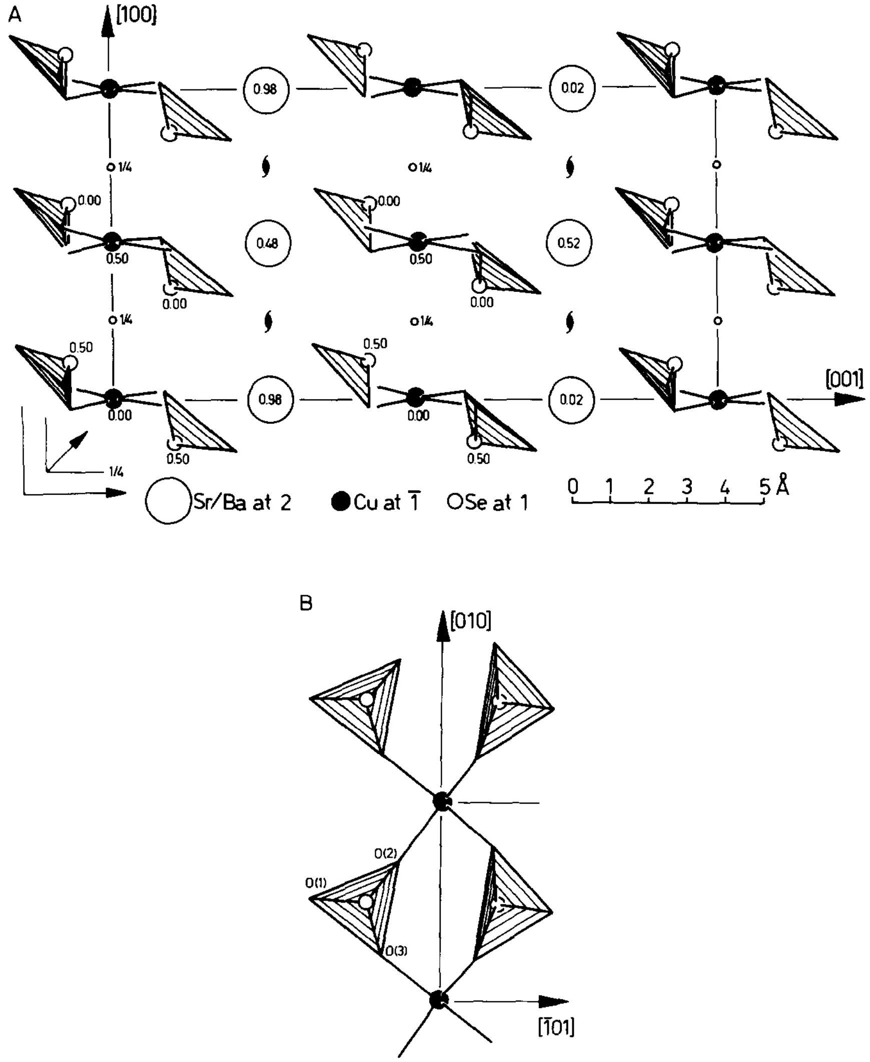

FIG. 3. The crystal structure of $BaCu(SeO_3)_2$-III (resp. $SrCu(SeO_3)_2$) (A) in a projection parallel [010]; (B) one of the $Cu(SeO_3)_2$ rows. Fractional atomic coordinates *y*/*b* and symmetry elements are indicated.

TABLE VI

SPACE-FILLING POLYHEDRA OF (a) THE ALKALINE EARTH ATOMS AND (b) THE O ATOMS (THE RATIOS OF ALL THE ATOMS ARE SET EQUAL TO 1.0; CALCULATIONS WERE PERFORMED WITH THE PROGRAM KRISTALLCHEMIE (*22*))

	$BaCu(SeO_3)_2$-I	$BaCu(SeO_3)_2$-II	$BaCu(SeO_3)_2$-III	$SrCu(SeO_3)_2$
	(a) Alkaline earth atoms			
Volume of the space-filling polyhedra [Å^3]	20.68	18.71	19.11	16.05
No. of faces[a] resulting from				
O atoms	11 (100–39%)	11 (100–45%)	10 (100–45%)	10 (100–22%)
Se atoms	2 (38–8%)	3 (≤1%)	0	0
Cu atoms	1 (≤1%)	1 (3%)	0	0
Coordination numbers referred to				
Hoppe (*20*)	8.1	8.2	7.5	7.2
O'Keeffe (*21*)	8.4	8.2	7.5	7.2

(b) O atoms (volumes of the space-filling polyhedra in Å^3)

$BaCu(SeO_3)_2$-I	O(11)	15.91	$BaCu(SeO_3)_2$-II	O(11)	15.19	$BaCu(SeO_3)$-III	O(1)	19.63
	O(12)	22.97		O(12)	16.12		O(2)	16.68
	O(21)	17.49		O(13)	15.75		O(3)	16.63
						Mean: 17.65		
	O(22)	13.76		O(21)	14.00	$SrCu(SeO_3)_2$	O(1)	17.79
	O(31)	14.16		O(22)	13.94		O(2)	15.63
	O(32)	13.39		O(23)	20.06		O(3)	15.73
	O(33)	18.05						
Mean: 16.53			Mean: 15.84			Mean: 16.38		

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[a] Range of percentages referred to area of largest face within each polyhedron in parentheses.

The structure type of $BaCu(SeO_3)_2$-III (Fig. 3) is principally different from the two other polymorphs. Here CuO_4 "squares" are connected by the selenite groups to form chains parallel [010] with the Ba atoms in between. The average Se–O and Cu–O bonds in $SrCu(SeO_3)_2$ are somewhat larger than in the isotypic $BaCu(SeO_3)_2$-III.

A geometrical analysis of the coordination polyhedra of the alkaline earth atoms and the O atoms seems to be of interest for a detailed comparison of the three structure types. For $BaCu(SeO_3)_2$-I and -II the formal coordination numbers according to Hoppe (*20*) and to O'Keeffe (*21*) are ~8.2, but for $BaCu(SeO_3)_2$-III only 7.5 and for $SrCu(SeO_3)_2$ 7.2 (see Table VI). It should be mentioned that only in $BaCu(SeO_3)_2$-I and -II are the Se and Cu atoms involved in building the space-filling polyhedra, indicating the requirement of a larger cation. Nevertheless, the volumes for all three of the Ba atoms in the title compound compare well to each other.

The volumes of the space-filling polyhedra of the O atoms give widely spreading values. It is conspicuous that in $BaCu(SeO_3)_2$-I and -II some of them are definitely smaller than in $BaCu(SeO_3)_2$-III. Considering the effective ionic radii (*23*) of Sr [10] (1.36 Å) and Ba [10] (1.52 Å) the substitution of the Ba atoms by Sr atoms in $BaCu(SeO_3)_2$-I and -II seems to be rather unlikely. As a consequence repeated trials to synthesize these two Sr compounds failed until now under the chosen conditions.

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