

Crystal Chemistry of Two Monoclinic Modifications of $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4$

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Two modifications of hydrothermally synthesized $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4$ crystallize in space group $P2_1/c$: the cell dimensions are $a=4.440(1)$, $b=15.852(4)$, $c=8.094(2)$ Å, $\beta=94.95(3)^\circ$ and $a=10.513(2)$, $b=7.224(3)$, $c=8.160(3)$ Å, $\beta=110.60(2)^\circ$; $Z=2$. The crystal structures were refined from 2067 observed X-ray reflections to $R=0.029$, $R_w=0.033$ and from 2100 observed reflections to $R=0.046$, $R_w=0.037$. The irregular coordination around the Bi^{III} atoms is caused by the lone-pair electrons, the Cu^{II} atoms are planar [4] coordinated; the $\text{Se}^{\text{IV}}\text{O}_3$ groups form the usual trigonal pyramids. Distinguishing features are $\text{Bi}_2(\text{SeO}_3)_2$ layers, which are interconnected in the two structures by $\text{Cu}(\text{SeO}_3)_2$ chains and $\text{Cu}(\text{SeO}_3)_2$ layers, respectively.

Like other transition metals copper(II) forms several selenites(IV). The mineral chalcomenite, orthorhombic $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$,¹ was the first phase out of this group of compounds for which the crystal structure was determined. During recent years a number of copper-selenites(IV) have been structurally investigated. Crystal structures of bismuth–copper-selenites are almost unknown; the only published structure, and moreover the only selenite(IV) compound containing Bi^{III} atoms, was that of the mineral francisite, $\text{BiCu}_3\text{O}_2\text{Cl}(\text{SeO}_3)_2$.² For the Bi^{III} -selenates(VI) $\text{Bi}(\text{OH})(\text{SeO}_4) \cdot \text{H}_2\text{O}$ and $(\text{BiO})_2(\text{SeO}_4) \cdot \text{H}_2\text{O}$ see Refs. 3 and 4.

Syntheses in the system $\text{Bi}_2\text{O}_3\text{–CuO–SeO}_2\text{–H}_2\text{O}$ produced three new $\text{Bi}^{\text{III}}\text{–Cu}^{\text{II}}$ -selenites(IV). Two isochemical compounds are structurally characterized in this paper; according to their structural features one- and two-dimensional $\text{Cu}(\text{SeO}_3)_2$ -units they are denoted $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-I}$ and $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-II}$, respectively. The crystal structure of $(\text{Bi}_2\text{O})\text{Cu}(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ will be published elsewhere.

Experimental

Syntheses were performed under hydrothermal conditions in steel vessels lined with teflon. Mixtures of equimolar amounts of Bi_2O_3 and CuO were inserted; an aqueous solution of H_2SeO_3 served as the solvent. The vessels were heated to 503 K for 3 days and cooled to room temperature with a cooling rate of 1 K h^{-1} . Besides $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-I}$ and $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-II}$ the following compounds were observed in different runs: $\text{CuSeO}_3\text{-III}^5$, $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$,^{1,6–8} $\text{Cu}[\text{SeO}_2(\text{OH})]_2$,⁹ and $(\text{Bi}_2\text{O})\text{Cu}(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$.

After checks by Weissenberg-film techniques single crystals suitable for structure investigations were selected for X-ray diffractometer measurements. Numerical absorption corrections were applied according to the crystal shape by Gaussian integration based on the length of the X-ray path through the sample. The structures were solved by Patterson and Fourier summations. Relevant data are summarized in Table 1, structural parameters are given in Table 2. The highest peaks in the final difference-Fourier summation are in the surroundings of the Bi atoms. Interatomic bond lengths, bond angles and bond valences are compiled in Table 3.

Results and discussion

The structure types of $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-I}$ and -II (Figs. 1 and 2) are distinct from each other, but they show some similarities with respect to the individual coordination of the cations (Table 3), to parts of the connection schemes and they have the same space group symmetry. Both compounds exhibit each one position for the Bi and Cu atoms, and two crystallographically different selenite groups. The Cu atoms have point symmetry $\bar{1}$; all the other atoms are on general positions. Both title compounds are formed by $\text{Bi}_2(\text{Se}(2)\text{O}_3)_2$ layers which are corner-connected to $\text{Cu}(\text{Se}(1)\text{O}_3)_2$ chains and $\text{Cu}(\text{Se}(1)\text{O}_3)_2$ layers, respectively.

In both compounds the bismuth atoms are *tri*-valent as indicated by the distribution of the Bi–O bond lengths and as supported by bond valence calculations.¹⁵ The coordination numbers are [5 + 4] for $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-I}$ and [4 + 5] for $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-II}$; the short bonds are arranged at one side of the Bi atoms to satisfy the space require-

Table 1. Summary of crystal data, X-ray data collection and structure refinements. A STOE AED 2 four-circle diffractometer (Mo tube, graphite monochromator) was used for data collection.

| Compound | $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-I}$ | $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-II}$ |
|---|---|--|
| $a/\text{\AA}$ | 4.440(1) | 10.513(4) |
| $b/\text{\AA}$ | 15.852(4) | 7.224(3) |
| $c/\text{\AA}$ | 8.094(2) | 8.160(3) |
| $\beta/^\circ$ | 94.95(3) | 110.60(2) |
| $V/\text{\AA}^3$ | 567.6 | 580.1 |
| Space group | $P2_1/c$ | $P2_1/c$ |
| Z | 2 | 2 |
| Reflections for cell parameter | 66 | 62 |
| Range of reflections/ $^\circ$ | $30.6 \leq 2\theta \leq 38.4$ | $25.1 \leq 2\theta \leq 42.2$ |
| $\rho_{\text{calc}}/\text{g cm}^{-3}$ | 5.79 | 5.66 |
| Crystal dimensions/ mm^3 | $0.30 \times 0.21 \times 0.13$ | $0.26 \times 0.12 \times 0.09$ |
| Crystallographic forms | {001}, {011}, {010}, {110}, {121}, {111} | {100}, {110}, {010}, {001}, {011} |
| Scan speed ($2\theta/\omega$ scan mode)/ $^\circ \text{ min}^{-1}$ | 0.90–3.60 | 0.90–1.80 |
| Scan width (+ α_1 - α_2 dispersion)/ $^\circ$ | 0.72 | 0.69 |
| Background correction | 0.21 $^\circ$ each side of the peak | 0.21 $^\circ$ each side of the peak |
| Maximal variation of intensity | $\pm 3\%$; 3 standards each 2 h | $\pm 3\%$; 3 standards each 2 h |
| Range of data collection/ $^\circ$ | $4 < 2\theta < 70$ | $4 < 2\theta < 70$ |
| $\mu(\text{MoK}\alpha)/\text{cm}^{-1}$ | 470 | 459 |
| Empirical absorption correction | Gaussian integration | Gaussian integration |
| Transmission factors | 0.016–0.075 | 0.011–0.066 |
| Total measured reflection | 6286 | 8306 |
| Observed unique reflections | 2475 | 2502 |
| Reflections used for refinements | 2067, $F_o > 4\sigma(F_o)$ | 2100, $F_o > 3\sigma(F_o)$ |
| R_{int} | 0.047 | 0.050 |
| R | 0.029 | 0.046 |
| R_w | 0.033 | 0.037 |
| w | $0.772 [\sigma(F_o)]^{-2}$ | $1.673 [\sigma(F_o)]^{-2}$ |
| Variable parameters | 89 | 89 |
| Max Δ/σ | ≤ 0.001 | ≤ 0.001 |
| Final difference Fourier map/ $e \text{\AA}^{-3}$ | -4.0 to +2.7 | -5.1 to +4.6 |

Data were corrected for Lorentz and polarization effects; neutral atomic complex scattering functions were from Ref. 10; programs SDP¹¹ and SHELX76¹² were used.

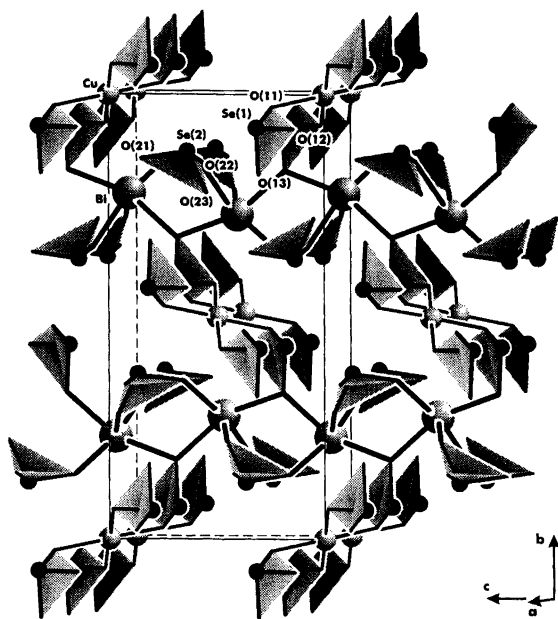


Fig. 1. The crystal structure of $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-I}$ in a projection slightly inclining to the (100) plane (program ATOMS,¹⁴ figure modified).

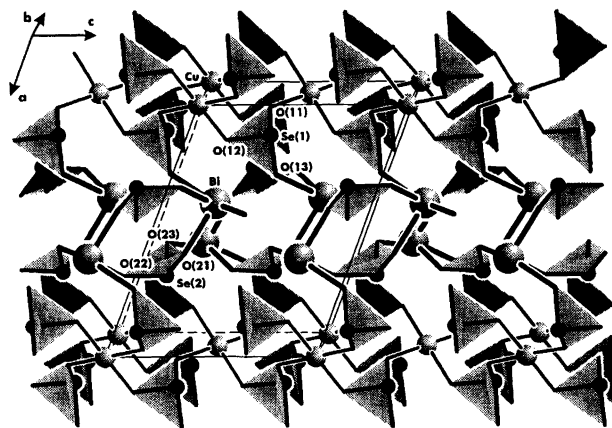


Fig. 2. The crystal structure of $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-II}$ in a projection slightly inclining to the (010) plane (program ATOMS,¹⁴ figure modified).

ments of the lone-pair electrons. Further neighbours are Se atoms with $\text{Bi-Se} > 3.3 \text{\AA}$. Considering short Bi-O bonds only, the Bi atoms are connected to chains parallel [001] in $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-I}$; in $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-II}$ the Bi atoms are not connected among each other by the short bonds. The BiO_9 polyhedra are connected to layers parallel (010) in $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-I}$ and parallel (100) in Bi_2Cu

Table 2. Structural parameters (with e.s.d.s in parentheses).

| Atom | X | Y | Z | U ₁₁ | U ₂₂ | U ₃₃ | U ₂₃ | U ₁₃ | U ₁₂ | B _{eq} |
|---|-------------|-------------|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Bi₂Cu(SeO₃)₄-I | | | | | | | | | | |
| Bi | 0.50023(6) | 0.22643(2) | 0.03190(3) | 0.0078(1) | 0.0093(1) | 0.0062(1) | -0.0001(1) | 0.0006(1) | 0.0000(1) | 0.61 |
| Cu | 0.0 | 0.0 | 0.0 | 0.0074(5) | 0.0149(6) | 0.0087(5) | 0.0016(1) | 0.0011(4) | -0.0018(4) | 0.81 |
| Se(1) | 0.45076(15) | 0.43137(5) | 0.24961(8) | 0.0076(3) | 0.0092(3) | 0.0045(2) | 0.0002(1) | -0.0012(2) | 0.0015(1) | 0.57 |
| Se(2) | 0.02083(15) | 0.12828(4) | 0.35588(8) | 0.0055(3) | 0.0083(3) | 0.0047(2) | 0.0000(1) | -0.0010(2) | -0.0008(2) | 0.49 |
| O(11) | 0.7974(12) | 0.4749(4) | 0.2796(6) | 0.011(2) | 0.018(3) | 0.011(2) | -0.0005(5) | 0.005(2) | -0.004(2) | 1.01 |
| O(12) | 0.333(12) | 0.4296(3) | 0.4435(6) | 0.012(2) | 0.012(2) | 0.008(2) | 0.0003(5) | 0.004(2) | 0.003(2) | 0.83 |
| O(13) | 0.5324(14) | 0.3249(4) | 0.2500(6) | 0.032(3) | 0.009(2) | 0.006(2) | -0.0002(5) | 0.004(2) | 0.003(2) | 1.22 |
| O(21) | -0.0808(13) | 0.1441(4) | 0.1638(6) | 0.015(3) | 0.025(3) | 0.007(2) | 0.0012(6) | -0.004(2) | 0.009(2) | 1.26 |
| O(22) | 0.4020(12) | 0.1504(4) | 0.3758(7) | 0.008(2) | 0.014(3) | 0.022(3) | -0.0022(6) | -0.001(2) | 0.000(2) | 1.15 |
| O(23) | -0.0566(12) | 0.2219(4) | 0.4542(7) | 0.008(2) | 0.015(3) | 0.019(2) | -0.0026(6) | 0.003(2) | 0.000(2) | 1.08 |
| Bi₂Cu(SeO₃)₄-II | | | | | | | | | | |
| Bi | 0.40057(4) | 0.11989(5) | 0.24927(5) | 0.0200(1) | 0.0116(1) | 0.0111(1) | 0.0006(1) | 0.0034(1) | 0.0003(1) | 1.17 |
| Cu | 0.0 | 0.0 | 0.0 | 0.0185(8) | 0.0237(10) | 0.0083(8) | -0.0012(4) | 0.0018(3) | -0.0037(3) | 1.39 |
| Se(1) | 0.13116(10) | 0.15738(15) | 0.38820(13) | 0.0186(4) | 0.0212(6) | 0.0106(4) | -0.0022(2) | 0.0033(1) | -0.0011(2) | 1.37 |
| Se(2) | 0.30821(10) | 0.66995(14) | 0.35609(12) | 0.0172(4) | 0.0126(5) | 0.0084(4) | 0.0007(2) | 0.0024(1) | -0.0005(2) | 1.05 |
| O(11) | 0.0427(9) | 0.3553(13) | 0.3328(11) | 0.036(5) | 0.054(7) | 0.017(4) | -0.007(2) | 0.000(2) | 0.014(2) | 3.02 |
| O(12) | 0.1492(7) | 0.1061(12) | 0.1931(9) | 0.022(3) | 0.034(5) | 0.009(3) | -0.006(2) | 0.003(1) | -0.004(1) | 1.75 |
| O(13) | 0.2935(7) | 0.2228(10) | 0.4795(10) | 0.019(3) | 0.022(4) | 0.014(3) | -0.006(2) | 0.002(1) | 0.000(1) | 1.52 |
| O(21) | 0.4082(8) | 0.5104(10) | 0.3083(10) | 0.033(4) | 0.011(3) | 0.025(4) | 0.001(2) | 0.009(2) | 0.000(1) | 1.84 |
| O(22) | 0.3107(8) | 0.6153(10) | 0.5585(9) | 0.041(4) | 0.014(4) | 0.015(3) | 0.004(2) | 0.008(1) | 0.003(2) | 1.89 |
| O(23) | 0.4210(8) | 0.8511(9) | 0.4140(9) | 0.027(4) | 0.013(4) | 0.013(3) | 0.003(2) | 0.001(1) | -0.002(1) | 1.50 |

The anisotropic displacement parameter is defined as: $\exp \left[-2\pi^2 \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} a_i^* a_j^* h_i h_j \right]$; B_{eq} is defined according to Ref. 13.

Table 3. Interatomic distances (in Å), bond angles (in °) and bond valence ν (in valence units; calculated according to Ref. 15); for the Cu and Se polyhedra bond angles (in °) and O–O edge lengths (in Å) are attached.

| | | | | | |
|---|----------|-----------------|---|----------|-----------|
| Bi₂Cu(SeO₃)₄-I | | | | | |
| Bi–O(23), ⁸ ν | 2.242(5) | 0.66 | Se(1)–O(11), ¹ ν | 1.685(5) | 1.41 |
| Bi–O(22), ⁶ ν | 2.345(6) | 0.50 | Se(1)–O(12), ¹ ν | 1.696(5) | 1.36 |
| Bi–O(13), ¹ ν | 2.351(5) | 0.49 | Se(1)–O(13), ¹ ν | 1.727(6) | 1.25 |
| Bi–O(13), ⁶ ν | 2.438(5) | 0.39 | \langle Se(1)–O \rangle , $\Sigma\nu$ | 1.703 | 4.02 |
| Bi–O(21), ³ ν | 2.442(6) | 0.39 | O(11), O(12) | 102.9(2) | 2.645(7) |
| Bi–O(23), ⁶ ν | 2.617(5) | 0.24 | O(11), O(13) | 102.2(3) | 2.655(8) |
| Bi–O(12), ⁶ ν | 2.662(5) | 0.21 | O(12), O(13) | 93.6(3) | 2.495(8) |
| Bi–O(22), ¹ ν | 3.098(6) | 0.07 | Se(2)–O(21), ¹ ν | 1.677(5) | 1.44 |
| Bi–O(21), ¹ ν | 3.158(5) | 0.06 | Se(2)–O(22), ¹ ν | 1.724(5) | 1.27 |
| $\Sigma\nu$ | | 3.01 | Se(2)–O(23), ¹ ν | 1.733(6) | 1.23 |
| Cu–O(11), ^{7,9} ν | 1.968(5) | 0.46 $2 \times$ | \langle Se(2)–O \rangle , $\Sigma\nu$ | 1.711 | 3.94 |
| Cu–O(12), ^{6,10} ν | 1.940(5) | 0.49 $2 \times$ | O(21), O(22) | 101.3(3) | 2.629(7) |
| \langle Cu–O \rangle , $\Sigma\nu$ | 1.954 | 1.90 | O(21), O(23) | 105.8(3) | 2.720(7) |
| O(11), O(12) | 88.2(2) | 2.719(7) | O(22), O(23) | 92.1(3) | 2.489(7) |
| O(11), O(12) | 91.8(2) | 2.807(7) | | | |
| Bi₂Cu(SeO₃)₄-II | | | | | |
| Bi–O(22), ⁶ ν | 2.273(7) | 0.61 | Se(1)–O(11), ¹ ν | 1.679(9) | 1.43 |
| Bi–O(23), ² ν | 2.329(7) | 0.52 | Se(1)–O(12), ¹ ν | 1.709(7) | 1.35 |
| Bi–O(21), ⁷ ν | 2.357(6) | 0.49 | Se(1)–O(13), ¹ ν | 1.672(6) | 1.46 |
| Bi–O(13), ⁶ ν | 2.379(7) | 0.46 | \langle Se(1)–O \rangle , $\Sigma\nu$ | 1.687 | 4.24 |
| Bi–O(12), ¹ ν | 2.520(5) | 0.31 | O(11), O(12) | 99.6(4) | 2.587(11) |
| Bi–O(13), ¹ ν | 2.615(6) | 0.24 | O(11), O(13) | 105.2(4) | 2.661(9) |
| Bi–O(23), ⁵ ν | 2.736(7) | 0.17 | O(12), O(13) | 92.6(3) | 2.445(10) |
| Bi–O(21), ¹ ν | 2.859(7) | 0.13 | Se(2)–O(21), ¹ ν | 1.695(7) | 1.37 |
| Bi–O(23), ⁷ ν | 3.138(6) | 0.06 | Se(2)–O(22), ¹ ν | 1.690(7) | 1.39 |
| $\Sigma\nu$ | | 2.99 | Se(2)–O(23), ¹ ν | 1.717(6) | 1.29 |
| Cu–O(11), ^{6,10} ν | 1.894(8) | 0.56 $2 \times$ | \langle Se(2)–O \rangle , $\Sigma\nu$ | 1.701 | 4.05 |
| Cu–O(12), ^{1,4} ν | 1.947(7) | 0.48 $2 \times$ | O(21), O(22) | 105.6(4) | 2.696(10) |
| \langle Cu–O \rangle , $\Sigma\nu$ | 1.920 | 2.08 | O(21), O(23) | 99.1(3) | 2.595(10) |
| O(11), O(12) | 87.8(3) | 2.664(11) | O(22), O(23) | 97.9(3) | 2.569(9) |
| O(11), O(12) | 92.2(3) | 2.767(11) | | | |

Symmetry code: ¹ x, y, z ; ² $x, -1+y, z$; ³ $1+x, y, z$; ⁴ $-x, -y, -z$; ⁵ $1-x, 1-y, 1-z$; ⁶ $x, 1/2-y, -1/2+z$; ⁷ $1-x, -1/2+y, 1/2-z$; ⁸ $1+x, 1/2-y, -1/2+z$; ⁹ $-1+x, 1/2-y, -1/2+z$; ¹⁰ $-x, -1/2+y, 1/2-z$.

(SeO₃)₄-II (Figs. 3a and 3b). In both compounds the BiO₉ polyhedra are predominantly coordinated to Se(2)O₃ groups: only three of the nine bonds are to Se(1)O₃ groups.

The Cu atoms are square-planar coordinated by O atoms of four Se(1)O₃ groups. The average \langle Cu–O \rangle bond lengths are 1.954 and 1.920 Å. The deviation of the O–Cu–O angles from rectangularity amounts to ca. 2°. In Bi₂Cu(SeO₃)₄-I two additional ligands have Cu–O(21) = 2.681(6) Å, indicating weak chemical interactions of the Cu atoms towards to the Bi₂(SeO₃)₂ layers. In Bi₂Cu(SeO₃)₄-II further neighbours to the Cu atom are four Se(1) and two O(22) atoms at ca. 3.2 Å. The CuO₄ squares are not connected to each other.

As usual the Se^{IV} atoms are pyramidally three-coordinated. The bond valences for the two Se atoms in Bi₂Cu(SeO₃)₄-I and for the Se(2) atom in Bi₂Cu(SeO₃)₄-II are well balanced (3.97–4.05 valence units), \langle Se–O \rangle is 1.701–1.711 Å. The bond valence of the Se(1) atom in Bi₂Cu(SeO₃)₄-II is overestimated (4.24 valence units); the average \langle Se(1)–O \rangle bond length of 1.687 Å belongs to the shortest known \langle Se–O \rangle values found bet-

ween 1.68 and 1.69 Å in the following compounds: Li₅Mn^{II}₄Mn^{III}(SeO₃)₈,¹⁶ Fe₂(SeO₃)₃·H₂O,¹⁷ K₂Co₂-(SeO₃)₃,¹⁸ Ni₃(SeO₃)₃·H₂O,^{19,20} Sr₂Cu(SeO₃)₃,²¹ Pb₂Cu₃O₂(NO₃)₂(SeO₃)₂,²² NaY(SeO₃)₂,²³ Cd(SeO₃) (mP40),²⁴ Cd₄(SeO₃)₄·3H₂O,²⁴ NaLa(SeO₃)₂,²³ and Pr₂(SeO₂OH)₂(SeO₃)₂.²⁵ The bond valences for the O atoms vary from 1.84 to 2.16 valence units.

Within the Cu(SeO₃)₂ chains of Bi₂Cu(SeO₃)₄-I and within the Cu(SeO₃)₂ layers of Bi₂Cu(SeO₃)₄-II the four corners of the CuO₄ squares are connected to four Se(1)O₃ pyramids. Each selenite pyramid is corner connected to two CuO₄ squares; one of these corners and the third corner link to the Bi₂(Se(2)O₃)₂ layers (Figs. 3c and 3d). These two connection types are well known: topologically the same Cu(SeO₃)₂ chains were found in the two isotypic compounds SrCu(SeO₃)₂,²⁶ and BaCu(SeO₃)₂,²⁶ as well as in Sr₂Cu(SeO₂OH)₂-(SeO₃)₂,²¹ (the SeO₂OH groups are not connected to the Cu atoms); the Cu atoms always have $\bar{1}$ symmetry. Worth mentioning is the similarity with the diselenite CuSe₂O₅:²⁷ here chains are formed by corner connection of square-planar coordinated Cu atoms of site symmetry

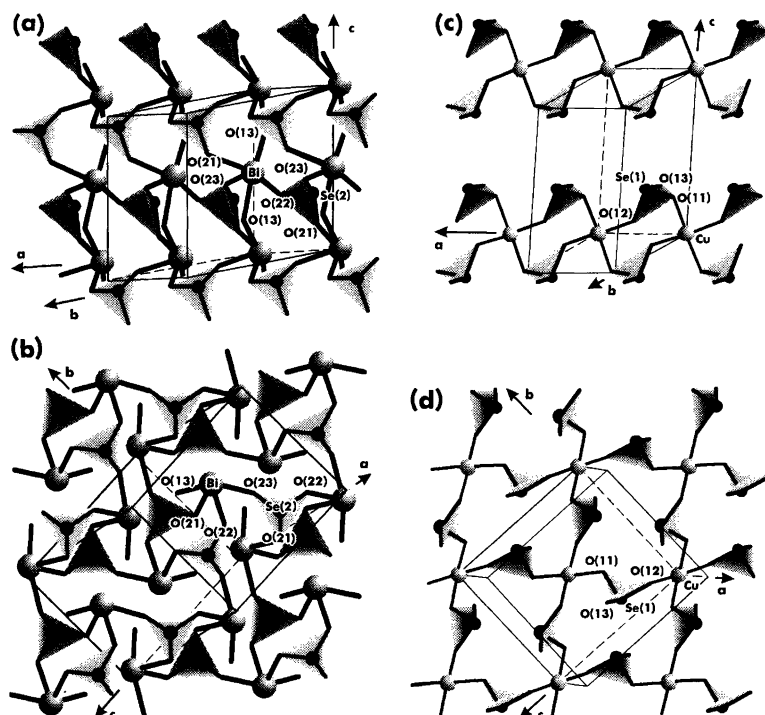


Fig. 3. Structural details: (a) the $\text{Bi}_2(\text{SeO}_3)_2$ layer in $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-I}$, (b) the $\text{Bi}_2(\text{SeO}_3)_2$ layer in $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-II}$, (c) the $\text{Cu}(\text{SeO}_3)_2$ chain in $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-I}$ and (d) the $\text{Cu}(\text{SeO}_3)_2$ layer in $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-II}$ (program ATOMS,¹⁴ figure modified).

$\bar{1}$ and Se_2O_5 dimers; formally the Se_2O_5 dimers are formed by sharing the O(13) corners between two $\text{Se}(1)\text{O}_3$ pyramids in $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-I}$. The translation period in the direction of the $\text{Cu}(\text{SeO}_3)_2$ chains is 5.13–5.26 Å in the earth alkaline-copper-selenites, in the title compound the CuO_4 squares are twisted to shorten the translation period to 4.44 Å. In CuSe_2O_5 the diselenite groups alternately point up and down, which once more shortens the translation period: 2×3.98 Å.

The $\text{Cu}(\text{SeO}_3)_2$ layers of $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-II}$ are comparable to layers with protonated selenite anions found in $\text{Cu}(\text{SeO}_2\text{OH})_2$,⁹ $\text{Cu}(\text{SeO}_2\text{OH})_2 \cdot \text{H}_2\text{O}$,²⁸ $\text{Fe}(\text{SeO}_2\text{OH})_3$,²⁹ $\text{Co}(\text{SeO}_2\text{OH})_2 \cdot 2\text{H}_2\text{O}$ ^{30–32} and $(\text{NH}_4)\text{Mn}(\text{SeO}_2\text{OH})_3$.³³ In these compounds the coordination number of the Cu atoms is [4+2], and the cations Fe, Co, and Mn are octahedrally six-coordinated; the two additional ligands point off the $\text{Me}(\text{SeO}_2\text{OH})_2$ layers. Each protonated selenite group bridges between two octahedra; the oxygen atom to which the hydrogen atom is bonded is unconnected. The layers are rectangular with the exception of $\text{Fe}(\text{SeO}_2\text{OH})_3$, where the monoclinic angle of 96.27° is within the layer. The shorter of the two cell parameters within the layer range, from 6.26 to 7.68 Å, the longer from 8.37 to 9.42 Å (recalculated for cells transformed analogously to that in $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-II}$, see Fig. 3d).

Within the $\text{Bi}_2(\text{SeO}_3)_2$ layers of the two title compounds all corners of the $\text{Se}(2)\text{O}_3$ groups are connected to one BiO_5 or BiO_4 configuration. In $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-I}$ the Bi atoms are sandwiched between the selenite groups. In $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-II}$ the Bi atoms are shifted towards to

the surface of the layers. The $\text{Bi}(\text{SeO}_3)_2$ layers are only somewhat thicker in $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-I}$ (3.86 Å) than in $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-II}$ (3.77 Å). The height of the $\text{Cu}(\text{SeO}_3)_2$ chains in $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-I}$ (5.55 Å) is smaller than the thickness of the $\text{Cu}(\text{SeO}_3)_2$ layers in $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-II}$ (5.78 Å). In $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-I}$ the $\text{Bi}(\text{SeO}_3)_2$ layers and the $\text{Cu}(\text{SeO}_3)_2$ chains are penetrating each other by 0.74 Å, in $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-II}$ different layers are separated from each other by a small amount (0.14 Å). In accordance, the compound $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-I}$ is more dense packed than $\text{Bi}_2\text{Cu}(\text{SeO}_3)_4\text{-II}$.

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