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[Cd₇(SeO₃)₈]{Cu₂Br₂}, a host-guest structure derived from β-CdSeO₃

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Abstract: A first cadmium copper selenite–bromide Cd₇Cu₂(SeO₃)₈Br₂ (**1**) was obtained via chemical vapor transport reactions. The new compound is triclinic, $P\bar{1}$, $a = 5.3280(5) \text{ \AA}$, $b = 10.6190(12) \text{ \AA}$, $c = 11.4380(13) \text{ \AA}$, $\alpha = 100.856(4)^\circ$, $\beta = 93.321(4)^\circ$, $\gamma = 91.021(4)^\circ$, $V = 634.22(12) \text{ \AA}^3$, $R_1 = 0.027$. **1** has no structural analogs and belongs to a new structure type. The structure of **1** can be described as a host-guest architecture. The host is the [Cd₇(SeO₃)₈]²⁻ interrupted framework, which consists of zigzag layers with a large aperture. The guests are copper bromide species. Thus, the formula can be written as [Cd₇(SeO₃)₈]{Cu₂Br₂}.

Keywords: cadmium; copper; halides; host-guest structures; chemical vapor transport

1 Introduction

The targeted synthesis of compounds possessing various physicochemical properties has been extensively utilized in recent decades, both for resolving practical issues and conducting fundamental research. One of the most successful approaches is based on the utilization of the stereochemical effect of ‘lone pair elements’ in intermediate oxidation states. The asymmetric environments thus formed promote the formation of porous and layered structures.^{1,2} The addition of halide anions can further enhance the formation of low-dimensional structures due to the so-called ‘chemical scissors’ effect, based on the electrostatic interaction between highly charged ‘lone pair’ cations and halide anions. The addition of magnetically active cations can lead to the formation of magnetic substructures with non-trivial architectures.^{3,4} The structural chemistry of cations such as Sn^{II}, Pb^{II}, Sb^{III}, Bi^{III}, Se^{IV}, Te^{IV}, and I^V is the most extensively investigated (e.g. Charkin et al.^{5,6}). Some representatives of

this group are found as minerals in nature, and synthetic approaches are simple. However, despite their abundance, these compounds have been studied sparsely. Particularly, compounds comprising the Cu²⁺ cation with cations of non-transition metals, such as yttrium, bismuth, or lead, have been extensively examined, whereas their analogs containing non-magnetic *d*-metal cations (e.g., Zn²⁺, Cd²⁺, Sc³⁺, Y³⁺, Zr⁴⁺, etc.) have received significantly less attention. The compounds CdCu₂(SeO₃)₂Cl₂⁷ and *MCu*₃(SeO₃)₂O₂X (*M* = Y, La; *X* = Cl, Br)^{8,9} have been reported recently. The mineral structure prototype for the latter is francisite BiCu₃(SeO₃)₂O₂Cl.¹⁰

Herein, we report on the synthesis and crystal structure of Cd₇Cu₂(SeO₃)₈Br₂, which belongs to a new structure type with a new host-guest architecture.

2 Experimental

2.1 Synthesis

Crystals of Cd₇Cu₂(SeO₃)₈Br₂ were obtained by the chemical vapor transport (CVT) reactions of cadmium selenite CdSeO₃ and copper bromide CuBr₂ (Vekton, 99.5%) in sealed quartz ampoules. Cadmium selenite was obtained by reacting selenous acid with a boiling solution of cadmium acetate, according to Gospodinov and Barkov.¹¹ The starting reagents were mixed in a molar ratio of 1:1 and placed in a 10 cm long quartz tube, which was further sealed under vacuum. The tube was placed in a Nabertherm furnace, with the cold end protruding 2–3 cm from the furnace. The tube was annealed at 400 °C for 48 h. Green crystals of the new compound Cd₇Cu₂(SeO₃)₈Br₂ were found in the cold zone of the tube.

Qualitative electron microprobe analysis (Hitachi TM3000) of Cd₇Cu₂(SeO₃)₈Br₂ crystals revealed no other elements, except Cd, Cu, Se and Br with atomic number greater than 11 (Na).

2.2 Single-crystal X-ray studies

A prismatic crystal of Cd₇Cu₂(SeO₃)₈Br₂ was mounted on a glass fiber and studied on a Rigaku Synergy-S X-ray diffractometer equipped with a micro-focus X-ray tube operating with MoK α radiation at 50 kV and 1 mA. More than a hemisphere of X-ray diffraction data was collected. The structure was solved by direct methods and refined using the SHELX software package. The new compound is triclinic, $P\bar{1}$, $a = 5.3280(5) \text{ \AA}$, $b = 10.6190(12) \text{ \AA}$, $c = 11.4380(13) \text{ \AA}$, $\alpha = 100.856(4)^\circ$, $\beta = 93.321(4)^\circ$, $\gamma = 91.021(4)^\circ$, $V = 634.22(12) \text{ \AA}^3$, $R_1 = 0.027$ (Table 1). Atom coordinates and bond-valence sums are given in Table 2 and selected interatomic distances are provided in Table 3. Bond-valence analysis was performed using bond-valence parameters taken from Gagné and Hawthorne¹² for

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Table 1: Crystallographic data and refinement parameters for Cd₇Cu₂(SeO₃)₈Br₂. Experiments were carried out at 100 K with MoK α radiation on Rigaku Synergy-S, CCD.

Space group	$P\bar{1}$
$a(\text{\AA})$	5.3280(5)
$b(\text{\AA})$	10.6190(12)
$c(\text{\AA})$	11.4380(13)
$\alpha(^{\circ})$	100.856(4)
$\beta(^{\circ})$	93.321(4)
$\gamma(^{\circ})$	91.021(4)
$V(\text{\AA}^3)$	634.22(12)
D_x (g/cm ³)	5.471
Crystal size, mm ³	0.10 × 0.20 × 0.20
θ max ($^{\circ}$)	28.774
Total reflections collected	4827
Unique reflections (R_{int})	3297(0.012)
Unique reflections $F > 4\sigma(F)$	3123
Weighting coefficients a, b	0.037700, 0.741400
Data/restraints/parameters	3123/0/200
R_1, wR_2	0.027, 0.066
R_1 all, wR_2 all	0.034, 0.068
S	1.037
$\rho_{max}, \min/e \text{\AA}^{-3}$	1.491/−1.149
CCDC	2339771

the Cd–O, Cu²⁺–O and Se⁴⁺–O bonds and from Brese and O’Keeffe¹³ for the Cd–Br, Cu²⁺–Br and Se⁴⁺–Br bonds. All of the Cd–O and Cd–Br bonds $\leq 3.20 \text{\AA}$, Se–O bonds $\leq 3.65 \text{\AA}$, Se–Br bonds $\leq 3.75 \text{\AA}$, Cu²⁺–O and Cu²⁺–Br $\leq 3.00 \text{\AA}$ were taken into consideration. All calculated bond-valence sums agree well with the expected oxidation states of all cations in Cd₇Cu₂(SeO₃)₈Br₂.

3 Crystal structure

The unique crystal structure of Cd₇Cu₂(SeO₃)₈Br₂ contains two Cu, four Cd, four Se, one Br, and 12 O sites (Table 2). Cu1 atom forms four very strong Cu–O_{eq} bonds ($\leq 2 \text{\AA}$) resulting in CuO₄ squares, which are complemented by two long Cu–O_{ap} bonds of 2.360(3) \AA each. The octahedron of Cu²⁺ can be described as [4 + 2] (Figure 1). The Cu2 also forms four strong Cu–O bonds, thus forming a square complemented by two apical Br[−] anions. As a result, an elongated CuO₄Br₂ octahedron is formed. This type of coordination is typical of mixed-ligand Cu²⁺ coordination polyhedra. The CuO₄Br₂ octahedra are strongly distorted. The Jahn-Teller effect^[14] is significantly more pronounced for mixed-ligand Cu₂O₄Br₂ octahedra than for Cu₁O₄O₂ octahedra in Cd₇Cu₂(SeO₃)₈Br₂.

Table 2: Atomic coordinates, displacement parameters (\AA^2) and bond-valence sums (in valence units (vu)) in Cd₇Cu₂(SeO₃)₈Br₂.

Atom	Wyck. site	B.V.S.	x	y	z	U_{eq}
Cd1	2i	2.08	0.45878(4)	0.38169(3)	0.17830(4)	0.01278(7)
Cd2	2i	1.90	0.05946(4)	0.83550(3)	−0.02125(4)	0.01411(8)
Cd3	1c	1.76	0	½	0	0.01663(11)
Cd4	2i	1.93	0.91543(5)	0.23887(3)	0.36109(4)	0.01256(7)
Cu1	1h	2.13	½	½	½	0.00927(15)
Cu2	1b	1.90	0	0	½	0.01086(16)
Se1	2i	4.07	0.99450(6)	0.52874(4)	0.33443(5)	0.00922(9)
Se2	2i	3.93	0.49925(6)	0.17655(4)	0.54795(5)	0.00988(9)
Se3	2i	4.10	0.53914(6)	0.71081(4)	0.10875(5)	0.00996(9)
Se4	2i	3.94	−0.38787(6)	0.91928(4)	−0.18600(5)	0.01115(10)
Br1	2i	0.50	0.99472(8)	0.12729(6)	0.74777(6)	0.02513(14)
O1	2i	2.10	0.0863(5)	0.4824(3)	0.1968(4)	0.0187(8)
O2	2i	2.05	0.1914(5)	0.4377(3)	0.4066(4)	0.0137(7)
O3	2i	2.12	0.7389(4)	0.4272(3)	0.3343(4)	0.0120(7)
O4	2i	2.01	0.5867(6)	0.3208(3)	0.5222(5)	0.0247(11)
O5	2i	2.03	0.2140(4)	0.1439(3)	0.4685(4)	0.0138(7)
O6	2i	1.98	0.6999(5)	0.0924(3)	0.4487(4)	0.0151(7)
O7	2i	1.98	0.5810(6)	0.5915(4)	0.1789(5)	0.0279(11)
O8	2i	2.18	0.7618(5)	0.6817(3)	0.0042(4)	0.0140(7)
O9	2i	1.99	0.2877(4)	0.6619(3)	0.0065(4)	0.0140(7)
O10	2i	2.00	−0.2634(5)	0.9724(3)	−0.0443(4)	0.0166(8)
O11	2i	2.08	−0.1862(5)	0.7947(3)	−0.2161(4)	0.0170(8)
O12	2i	1.99	−0.6450(5)	0.8239(3)	−0.1736(4)	0.0146(7)

Table 3: Selected interatomic distances (Å) in the structure of $\text{Cd}_7\text{Cu}_2(\text{SeO}_3)_8\text{Br}_2$.

Cd1–O3	2.233(4)	Cu1–O2	1.943(3) × 2
Cd1–O1	2.273(3)	Cu1–O4	2.025(3) × 2
Cd1–O7	2.308(4)	Cu1–O3	2.360(3) × 2
Cd1–O8	2.313(4)		
Cd1–O12	2.407(3)	Cu2–O5	1.989(3) × 2
Cd1–O11	2.467(3)	Cu2–O6	2.007(3) × 2
Cd1–O9	2.548(4)	Cu2–Br1	2.9030(7) × 2
Cd1–O2	3.013(4)		
		Se1–O1	1.663(4)
Cd2–O10	2.271(3)	Se1–O2	1.718(3)
Cd2–O9	2.288(3)	Se1–O3	1.722(3)
Cd2–O10	2.307(3)	Se1–O7	2.916(4)
Cd2–O8	2.325(3)	Se1–O4	2.947(4)
Cd2–O12	2.403(4)	Se1–O2	3.137(4)
Cd2–O11	2.479(4)		
Cd2–Br1	3.1092(9)	Se2–O4	1.676(3)
		Se2–O5	1.720(3)
Cd3–O9	2.270(3) × 2	Se2–O6	1.739(3)
Cd3–O1	2.314(4) × 2	Se2–O6	3.037(3)
Cd3–O8	2.322(3) × 2	Se2–Br1	3.5024(8)
Cd3–O7	3.158(5) × 2	Se2–O7	3.648(5)
		Se2–Br1	3.7197(7)
Cd4–O11	2.243(3)		
Cd4–O3	2.290(3)	Se3–O7	1.635(4)
Cd4–O5	2.314(3)	Se3–O8	1.724(3)
Cd4–O6	2.324(3)	Se3–O9	1.731(3)
Cd4–O12	2.488(4)	Se3–Br1	3.1828(7)
Cd4–O2	2.506(3)	Se3–Br1	3.6595(7)
Cd4–O4	2.654(4)		
		Se4–O10	1.703(4)
		Se4–O11	1.716(3)
		Se4–O12	1.717(3)
		Se4–Br1	3.2026(7)
		Se4–O6	3.329(4)
		Se4–O10	3.349(4)

Cadmium atoms have irregular coordination environments in $\text{Cd}_7\text{Cu}_2(\text{SeO}_3)_8\text{Br}_2$, which is consistent with the $\text{Cd } 4d^{10}$ configuration. Cd1 is coordinated by eight oxygen atoms at $\leq 3 \text{ \AA}$. The Cd2 coordination environment is strongly asymmetrical, with six oxygen atoms in one coordination hemisphere and one Br^- anion in the other (Figure 1). The coordination of the Cd3 atom can be described as octahedral, with the formation of two additional long Cd3–O7 bonds at 3.158(5) Å. Cd4 forms irregular Cd4O₇ polyhedra similar to those in the structure of monoclinic CdSeO_3 .¹⁵

Each of four Se atoms forms three nearly equal $\text{Se}^{4+}\text{--O}$ bonds (Table 3) in the range 1.635(4) – 1.739(3) Å and occupies an apex of a SeO_3 pyramid. This one-sided pyramidal configuration is typical of a Se^{4+} cation.

CdO_n polyhedra share with each other via common edges and corners, thus forming zigzag layers, as shown in Figure 2a. All oxygen atoms are shared with the SeO_3 groups

which decorate the layers. There are vacancies in the layer, each corresponding to the removed cadmium atom (Figure 2b). The role of the vacancies is likely to reduce the structural strain due to the strong corrugation of the layer. $[\text{Cd}_7(\text{SeO}_3)_8]^{2-}$ layers are interconnected via Cu^{2+} -centered polyhedra (Figure 2a,c) into a $[\text{Cd}_7\text{Cu}_2(\text{SeO}_3)_8]^{2+}$ porous framework with channels elongated along the *a* axis and occupied by Br^- anions. Smaller “empty” channels are formed along the *c* axis (Figure 2d). The selenite groups are directed towards each other and the bromine anion, thereby demonstrating the phenomenon of halophilicity. The Se3 and Se4 atoms form relatively strong Se–Br bonds of $\sim 0.1 \text{ v.u.}$ each, while Se1 does not (Table 3). The Se2 atom forms weak Se2–Br1 bonds. The Se–Br interactions seem to be important for the stabilization of the structural architecture of $\text{Cd}_7\text{Cu}_2(\text{SeO}_3)_8\text{Br}_2$.

4 Discussion

The archetype of the structural architecture of $\text{Cd}_7\text{Cu}_2(\text{SeO}_3)_8\text{Br}_2$ is the structure of monoclinic CdSeO_3 ($\beta\text{-CdSeO}_3$).¹⁵ The latter is a three-dimensional framework containing cavities with a similar geometry and decorated with ‘lone pair’ Se^{4+} cations. The structure of $\text{Cd}_7\text{Cu}_2(\text{SeO}_3)_8\text{Br}_2$ can be obtained from the ideal $\beta\text{-CdSeO}_3$ according to the following sequential transformations (Figure 3): (1) incorporation of Br atoms into the cavities in the $\beta\text{-CdSeO}_3$ framework; (2) replacement of the part of Cd^{2+} cations in the $\beta\text{-CdSeO}_3$ framework by Cu^{2+} Jahn-Teller cations; (3) lowering of the symmetry to triclinic and strong distortion of cadmium coordination to reduce the stress induced by the insertion of Br^- anions and Cu^{2+} cations. The diversity of the Cd^{2+} coordination environments in $\text{Cd}_7\text{Cu}_2(\text{SeO}_3)_8\text{Br}_2$ is striking. There exist two coordinations, namely Cd1O₈ and Cd4O₇, which bear a resemblance to the structure of $\beta\text{-CdSeO}_3$, and a more symmetric counterpart, namely Cd3O₆, similar to those in the structure of orthorhombic $\alpha\text{-CdSeO}_3$.

The structure of $\text{Cd}_7\text{Cu}_2(\text{SeO}_3)_8\text{Br}_2$ can be described as a host-guest architecture. The host is the cadmium-selenite interrupted framework, which consists of zigzag layers with a large aperture. The guests are divalent copper cations and CuBr_2 groups. Thus, the formula can be written as $[\text{Cd}_7(\text{SeO}_3)_8]\{\text{Cu}_2\text{Br}_2\}$. Host-guest structures are characteristic of compounds crystallizing via CVT reactions^{16,17} and minerals formed from a gas in volcanic fumaroles.¹⁸

To date, two cadmium-copper selenite halides are known: $\text{CdCu}_2(\text{SeO}_3)_2\text{Cl}_2$ ⁷ and $\text{Cd}_7\text{Cu}_2(\text{SeO}_3)_8\text{Br}_2$ (this work). The presence of cadmium atoms with an irregular and flexible environment ($4d^{10}$, CFSE = 0) in combination with SeO_3 groups results in the formation of large cavities and the

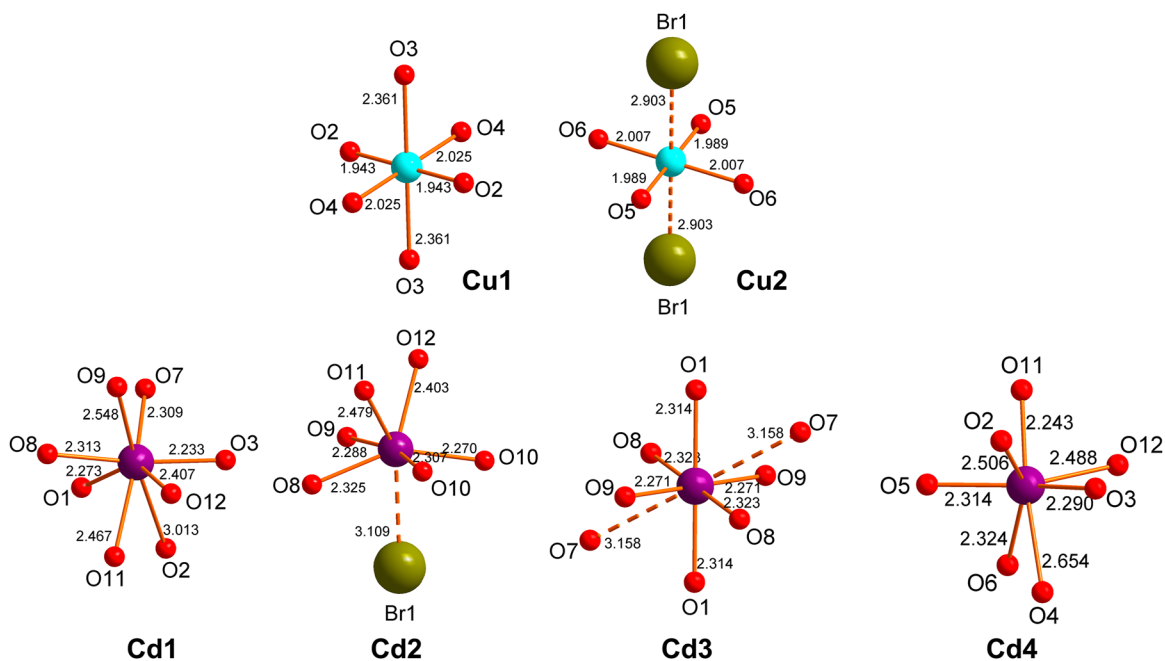


Figure 1: Coordination of atoms in the structure of $\text{Cd}_7\text{Cu}_2(\text{SeO}_3)_8\text{Br}_2$.

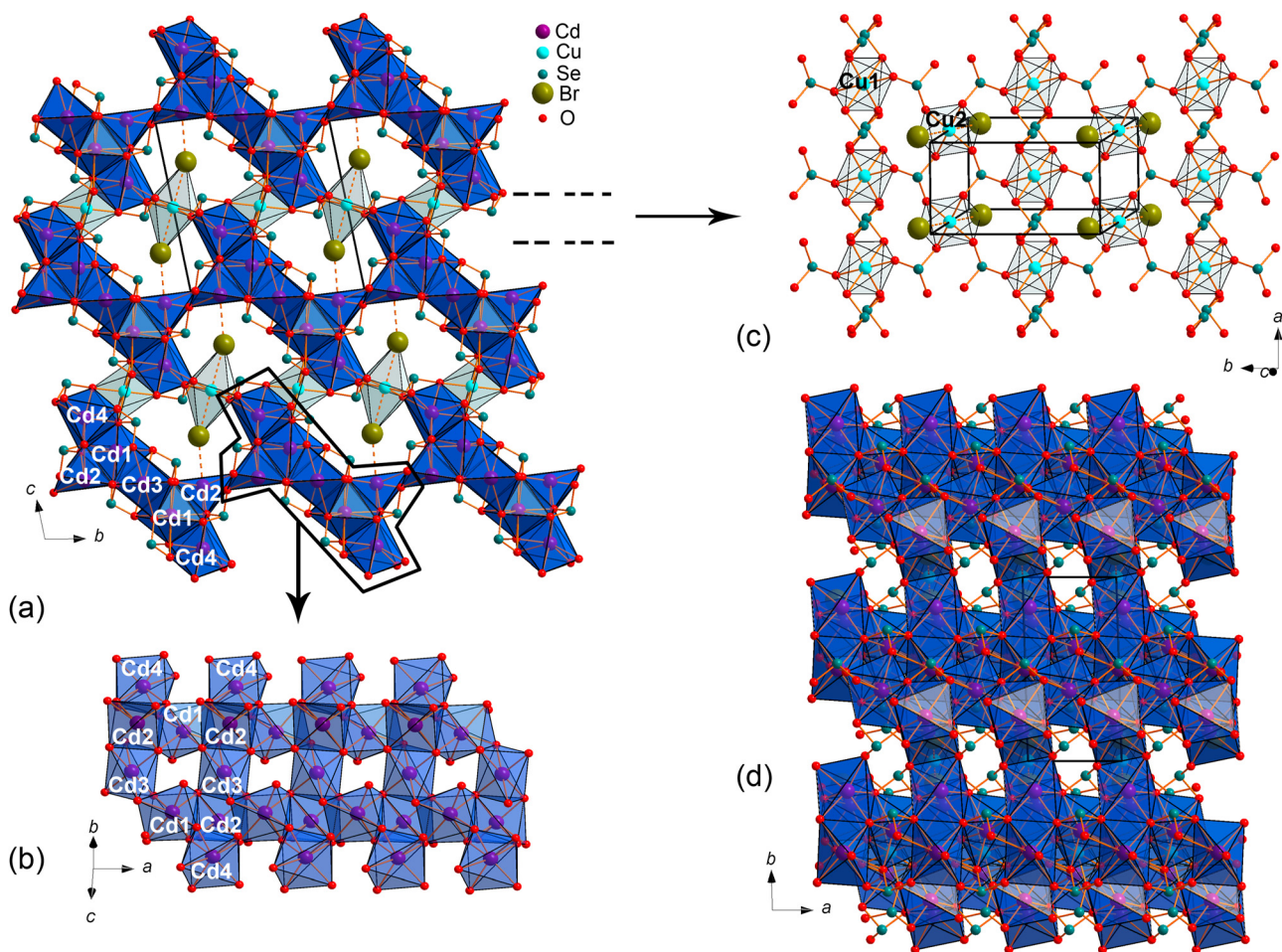


Figure 2: General projection of the crystal structure of $\text{Cd}_7\text{Cu}_2(\text{SeO}_3)_8\text{Br}_2$ along the a axis (a). Fragment of the $[\text{Cd}_7(\text{SeO}_3)_8]^{2-}$ zigzag layer (b). Arrangement of Cu-centered polyhedra interconnected via SeO_3 groups (c). General projection of the crystal structure of $\text{Cd}_7\text{Cu}_2(\text{SeO}_3)_8\text{Br}_2$ along the c axis (d).

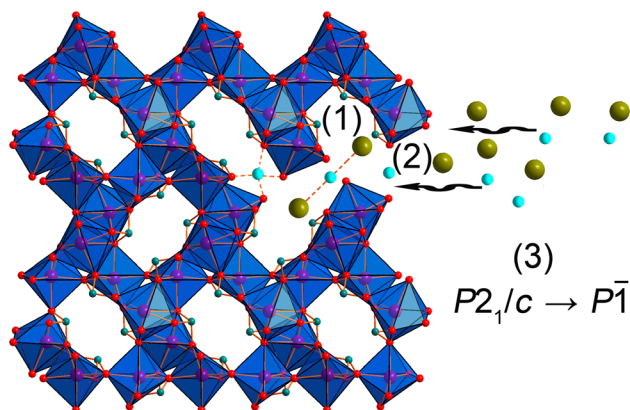


Figure 3: Imaginary scheme of the transformation from the ideal $\beta\text{-CdSeO}_3$ structure ($\text{CdO}_7 = \text{blue}$, $\text{SeO}_3 = \text{green}$) into $\text{Cd}_7\text{Cu}_2(\text{SeO}_3)_8\text{Br}_2$ via the following sequential transformations: (1) incorporation of Br atoms into the cavities in $\beta\text{-CdSeO}_3$; (2) replacement of the part of Cd^{2+} cations in the $\beta\text{-CdSeO}_3$ framework by the Cu^{2+} cations; (3) lowering of the symmetry to triclinic and strong distortion of cadmium coordination.

inclusion of the guest Cu–Br complexes in $\text{Cd}_7\text{Cu}_2(\text{SeO}_3)_8\text{Br}_2$. Cadmium forms a CdO_2Cl_4 octahedron surrounded by eight copper-centered polyhedra in a perovskite-like fashion in $\text{CdCu}_2(\text{SeO}_3)_2\text{Cl}_2$.⁷ Both structures belong to the $x\text{MSeO}_3:y\text{MX}_2$ series. To date, the most common $x:y$ ratios are 1:1, 2:1, and 4:1; the 8:1 ratio is observed for the first time. Further studies and CVT synthesis of cadmium selenite halides will significantly expand Cd(II) structural chemistry. The substitution of a Cd^{2+} cation with a magnetically active metal cation, such as Co^{2+} , can lead to the formation of compounds with unusual magnetic properties.

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