

Cd₃Se₃O₁₀, isotypic with its mercury analogue**Matthias Weil**

Institute for Chemical Technologies and Analytics, Division of Structural Chemistry, Vienna University of Technology, Getreidemarkt 9/164-SC, A-1060 Vienna, Austria

Correspondence e-mail: mweil@mail.zserv.tuwien.ac.at

Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{Se}-\text{O}) = 0.004\text{ \AA}$

R factor = 0.018

w R factor = 0.044

Data-to-parameter ratio = 17.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The mixed-valent $\text{Se}^{\text{IV/VI}}$ compound tricadmium(II) bis-[selenite(IV)] selenate(VI), $\text{Cd}_3(\text{SeO}_3)_2\text{SeO}_4$, contains three crystallographically inequivalent Cd^{II} cations, one $\text{Se}^{\text{VI}}\text{O}_4$ tetrahedron and two independent $\text{Se}^{\text{IV}}\text{O}_3$ pyramids corresponding to the formula $\text{Cd}_3(\text{SeO}_3)_2(\text{SeO}_4)$. The structure is composed of a three-dimensional network with channels extending parallel to the b axis. Distances and angles within the three $[\text{CdO}_x]$ polyhedra ($x = 6, 8$), as well as within the anionic framework, deviate only slightly from those of the isotypic mercury analogue, $\text{Hg}_3\text{Se}_3\text{O}_{10}$.

Received 14 November 2002

Accepted 21 November 2002

Online 30 November 2002

Comment

Numerous phases within the system $\text{Cd}-\text{Se}-\text{O}-(\text{H})$ are listed in standard handbooks about cadmium and its compounds (Gmelins Handbuch der Anorganischen Chemie, 1959), and most of these compounds have been crystallographically well characterized in the meantime. For the anhydrous selenites(IV) $\alpha\text{-CdSeO}_3$, $\beta\text{-CdSeO}_3$ (Valkonen, 1994a) and CdSe_2O_5 (Valkonen, 1994b), for the hydrous selenites(IV) $\text{CdSeO}_3(\text{H}_2\text{O})$ (Bäumer *et al.*, 1998), $\text{Cd}_3(\text{HSeO}_3)_2(\text{SeO}_3)_2$ (Valkonen, 1994b) and $(\text{CdSeO}_3)_4(\text{H}_2\text{O})_3$ (Valkonen, 1994a), as well as for the selenates(VI) $\text{CdSeO}_4(\text{H}_2\text{O})$ (Stålhandske, 1981), CdSeO_4 , $\text{Cd}(\text{HSeO}_4)_2(\text{H}_2\text{O})$ (Morozov *et al.*, 1999) and $\text{CdSeO}_4(\text{H}_2\text{O})_2$ (Weil, 2002), full structure analyses based on single-crystal data have been reported. Powder data are given for the tetraselenite(IV) $\text{Cd}_3\text{Se}_4\text{O}_{11}$ (Markovskii & Sapozhnikov, 1961).

$\text{Cd}_3\text{Se}_3\text{O}_{10}$ is reported for the first time and reveals isotypism with its mercury analogue, $\text{Hg}_3\text{Se}_3\text{O}_{10}$, whose

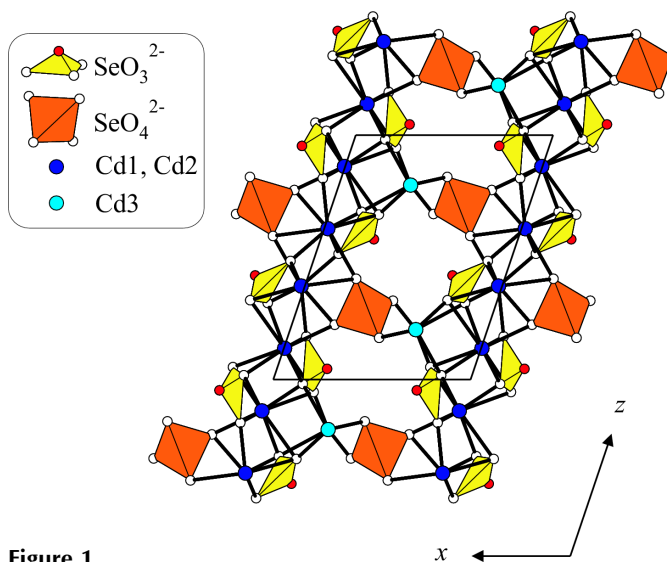


Figure 1
Projection of the crystal structure along $[010]$.

preparation and crystal structure were recently described in detail (Weil & Kolitsch, 2002). The crystal structure is composed of three independent Cd^{II} cations, two Se^{IV}O₃ groups and a Se^{VI}O₄ group as the main building units. Cd₃Se₃O₁₀ is the first Cd compound to contain both selenium(IV) and selenium(VI) oxo groups within the structure.

The building units are linked *via* common O atoms to form a three-dimensional network. Edge-sharing [CdO₈] polyhedra build layers ∞ [CdO_{8/2}] parallel to the *bc* plane, which are bridged by the Se^{IV}O₃ groups. Two adjacent layers are connected *via* Se^{VI}O₄ tetrahedra and [CdO₆] polyhedra along the *a* axis, to form channels extending parallel to the *b* axis, as depicted in Fig. 1. The selenite(IV) groups are situated above and below the cavities of the ∞ [CdO_{8/2}] layers, with the non-bonding orbitals directed towards each other into the cavities of the structure.

If bonding interactions are considered for distances $d(\text{Cd}-\text{O}) < 3.0 \text{ \AA}$, Cd1 and Cd2 are eight-coordinate with four short, two medium and two longer distances, resulting in a [4 + 2 + 2]-coordination with similar mean distances of $\bar{d}(\text{Cd1}-\text{O}) = 2.475 \text{ \AA}$ and $\bar{d}(\text{Cd2}-\text{O}) = 2.484 \text{ \AA}$. Cd3 shows a [4 + 2]-coordination, with a slightly shorter mean of $\bar{d}(\text{Cd3}-\text{O}) = 2.400 \text{ \AA}$.

Both selenite(IV) (Se1 and Se2) and selenate(VI) (Se3) groups display the well-known geometry of a trigonal pyramid [Se1: $\bar{d}(\text{Se1}-\text{O}) = 1.702 \text{ \AA}$, mean angle: 97.5°; Se2: $\bar{d}(\text{Se2}-\text{O}) = 1.704 \text{ \AA}$, mean angle 97.9°] and a tetrahedron [$\bar{d}(\text{Se3}-\text{O}) = 1.638 \text{ \AA}$, mean angle 109.5°], respectively.

The bond-valence sums, as calculated with the parameters given by Brese & O'Keeffe (1991), are in agreement with the expected values: Cd1 (CN = 8, 1.972), Cd2 (8, 2.082), Cd3 (6, 2.016), Se1 (3, 4.032), Se2 (3, 4.010), Se3 (4, 6.013), O1 (3, 2.133), O2 (3, 2.167), O3 (4, 2.099), O4 (4, 2.079), O5 (4, 2.163), O6 (4, 2.155), O7 (2, 1.892), O8 (2, 1.835), O9 (3, 1.787), O10 (3, 1.813). The O atoms which belong to selenite(IV) groups are O1–O6, and the O atoms of the selenate(VI) group are O7–O10.

Experimental

Experiments intended to prepare single crystals of compounds with the general formula (CdSeO₄)_x(HgO)_y(H₂O)_z, with *x* = 1, *y* = 1, 1.5 or 2 and *z* = 0 or 1 (Denk & Leschhorn, 1966), yielded colourless crystals, with mostly rod-like habit, of the title compound and colourless plates of composition (CdSeO₄)(HgO)(H₂O) [space group *P2*/*n*, *a* = 7.9895 (18) Å, *b* = 6.3307 (6) Å, *c* = 10.5738 (11) Å and β = 102.795 (2)°; Weil, 2002] by reacting HgO and CdSeO₄(H₂O)₂ in the molar ratio 1:2 in demineralized water under hydrothermal conditions (teflon-lined steel autoclave, 523 K, 6 d).

Crystal data

Cd₃(SeO₃)₂SeO₄
M_r = 734.08
 Monoclinic, *P2*₁
a = 8.3031 (8) Å
b = 5.3377 (5) Å
c = 10.8485 (11) Å
 β = 108.659 (2)°
V = 455.53 (8) Å³
Z = 2

D_x = 5.352 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 4083 reflections
 θ = 2.7–30.5°
 μ = 18.97 mm⁻¹
T = 293 (2) K
 Rod, colourless
 0.20 × 0.04 × 0.04 mm

Data collection

Siemens SMART diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
*T*_{min} = 0.116, *T*_{max} = 0.518
 4516 measured reflections
 2497 independent reflections

2402 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.023
 θ_{max} = 30.5°
h = -11 → 11
k = -7 → 7
l = -14 → 14

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.018
wR(*F*²) = 0.044
S = 1.00
 2497 reflections
 146 parameters
w = 1/[σ²(*F_o*²)]
 (Δ/σ)_{max} = 0.001

Δρ_{max} = 0.97 e Å⁻³
 Δρ_{min} = -0.79 e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0065 (3)
 Absolute structure: Flack (1983), 1443 Friedel pairs
 Flack parameter = 0.080 (9)

Table 1

Selected geometric parameters (Å, °).

Cd1–O3	2.258 (3)	Cd3–O6	2.132 (3)
Cd1–O1 ⁱ	2.287 (3)	Cd3–O5 ^{viii}	2.157 (3)
Cd1–O4 ⁱⁱ	2.307 (3)	Cd3–O8	2.250 (4)
Cd1–O4	2.327 (3)	Cd3–O7 ^{viii}	2.254 (4)
Cd1–O10 ⁱⁱⁱ	2.468 (4)	Cd3–O4	2.664 (3)
Cd1–O5 ^{iv}	2.545 (4)	Cd3–O3 ^{viii}	2.940 (3)
Cd1–O5	2.703 (4)	Se1–O1	1.694 (3)
Cd1–O6	2.902 (4)	Se1–O5 ^{ix}	1.696 (3)
Cd2–O2	2.191 (3)	Se1–O4 ^{ix}	1.715 (3)
Cd2–O1	2.235 (3)	Se2–O6	1.695 (3)
Cd2–O3 ⁱ	2.280 (3)	Se2–O2	1.700 (3)
Cd2–O2 ^v	2.286 (3)	Se2–O3	1.716 (3)
Cd2–O6 ^v	2.537 (4)	Se3–O9	1.624 (3)
Cd2–O9 ⁱⁱⁱ	2.551 (3)	Se3–O10	1.636 (3)
Cd2–O10 ^{vi}	2.814 (4)	Se3–O7	1.637 (3)
Cd2–O9 ^{vii}	2.980 (4)	Se3–O8	1.653 (3)
O1–Se1–O5 ^{ix}	94.02 (16)	O9–Se3–O10	112.29 (18)
O1–Se1–O4 ^{ix}	101.51 (16)	O9–Se3–O7	109.40 (18)
O5 ^{ix} –Se1–O4 ^{ix}	96.94 (16)	O10–Se3–O7	109.09 (19)
O6–Se2–O2	93.95 (16)	O9–Se3–O8	109.05 (19)
O6–Se2–O3	98.51 (17)	O10–Se3–O8	107.99 (18)
O2–Se2–O3	101.27 (17)	O7–Se3–O8	108.96 (17)

Symmetry codes: (i) $-x, \frac{1}{2} + y, 1 - z$; (ii) $-x, y - \frac{1}{2}, -z$; (iii) $x - 1, y, z$; (iv) $-x, \frac{1}{2} + y, -z$; (v) $-x, y - \frac{1}{2}, 1 - z$; (vi) $1 - x, \frac{1}{2} + y, 1 - z$; (vii) $1 - x, y - \frac{1}{2}, 1 - z$; (viii) $x, 1 + y, z$; (ix) $x, y, 1 + z$.

Systematic absences $k = 2n + 1$ for the (0*k*0) reflections and similar lattice parameters revealed isotypism with the mercury analogue, Hg₃Se₃O₁₀. The crystal structure was therefore refined with the atomic coordinates of the mercury compound as starting parameters. Refinement of the occupancy factors did not indicate any incorporation of Hg^{II} into the structure.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ATOMS for Windows (Dowty, 2000); software used to prepare material for publication: SHELXL97.

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