Crystal Structure of a New Modification of CoSeO₃

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The crystal structure of a hydrothermally synthesized new modification of $CoSeO_3$ ($CoSeO_3$-II) was determined by direct and Fourier methods using single-crystal X-ray diffraction data up to $\sin \theta/\lambda = 0.7$ Å^{-1} [monoclinic, space group $C2/c$, $a = 15.646(3)$ Å, $b = 9.947(2)$ Å, $c = 14.984(3)$ Å, $\beta = 110.65(1)°$, $Z = 32$; $R_w = 0.038$ for 2948 unique reflections with $F_o > 3\sigma(F_o)$]. The structure of $CoSeO_3$-II is built up from complex $\frac{2}{\infty}[Co_3(SeO_3)_4]$ sheets parallel to (100), which are composed of, in part, strongly distorted CoO_6 octahedra and pyramidal SeO_3 groups. These closely packed sheets are further linked by a less distorted type of CoO_6 octahedra. Individual Co–O and Se–O bond lengths within the four crystallographically different CoO_6 and SeO_3 polyhedra in $CoSeO_3$-II range from 2.018 to 2.344 Å and from 1.662 to 1.771 Å, respectively. The structure of $CoSeO_3$-II is closely related to that of $Co_3(SeO_3)_3 \cdot H_2O$. © 1995 Academic Press, Inc.

INTRODUCTION

Within the last two decades, a number of transition metal selenites with the general formula $Me(II)SeO_3$ have been structurally investigated. First, Kohn *et al.* (1) reported the high pressure synthesis and crystal structure of an isotypic series crystallizing in space group *Pnma* with the divalent metals, Me = Mn, Co, Ni, Cu, Zn (and also Mg), in octahedral coordination. Later, Bensch and Günter (2), Effenberger (3), and Hawthorne *et al.* (4) independently investigated a new structure type (space group *Pbca*) with a copper (3, 4) and zinc representative (2, 4), where the divalent cations are fivefold coordinated. Effenberger (3) also reported two additional new structure types for Cu SeO₃ (groups $P2_1/n$ and $P\bar{1}$), which are characterized by the strong Jahn–Teller distortion of the Cu(II) ions. Recently, Valkonen (5) determined the structures of two modifications of CdSeO₃, one of which belongs to the *Pnma* structure type mentioned above, the other one (space group $P2_1/c$) represents a new structure type with Cd(II) atoms in trigonal prismatic coordination.

The present paper reports the crystal structure investigation of a new modification of CoSeO₃ (space group $C2/c$), in the following denoted CoSeO₃-II. This structure is closely related to that of $Co_3(SeO_3)_3 \cdot H_2O$ (6), and both

are characterized by a strong distortion of their CoO_6 octahedra. This paper also continues a study on the crystal chemistry of Co(II)-selenites (6–13).

EXPERIMENTAL

Dark violet single crystals of CoSeO₃-II in sizes up to ~1 mm were obtained as the main crystalline product in synthesis experiments aiming at the preparation of Rb representatives of the $K_2Co(SeO_3)_2$, $K_2Co_2(SeO_3)_3$, and $K_2Co_2(SeO_3)_3 \cdot 2H_2O$ structures types (8–10). In these synthesis runs SeO_2, $Co(OH)_2$, RbOH and H_2O were inserted in varying molar ratios in teflon-lined steel vessels (capacity ~4–8 cm³, filling degree ~10–50%) and kept in the closed vessels at temperatures of 200–230°C for 4–12 days. It seems that—irrespective of the mentioned variation of experimental parameters—the presence of Rb⁺ ions in the primary solutions has a promotive effect on the formation of CoSeO₃-II, but no detailed investigations on this effect were made. However, in a series of further synthesis runs under the same experimental conditions, where Rb⁺ was omitted in the starting solutions or replaced by chemically related (e.g., K⁺, Cs⁺) or similarly sized cations (e.g., Ba⁺²), the formation of CoSeO₃-II could not be observed.

Single-crystal X-ray diffraction intensities of CoSeO₃-II up to $\sin \theta/\lambda = 0.7$ Å^{-1} were measured on a Stoe four-circle diffractometer AED2 using graphite monochromatized Mo$K\alpha$ radiation (2θ–ω scans, 35 steps/reflection, increased for α_1–α_2 splitting, 2 × 5 steps for background correction, 0.03°, and 0.5–1.5 sec/step; three standard reflections each 120 min; lattice parameters refined from 38 accurate 2θ values in the range $36° < 2\theta < 44°$). Corrections for Lorentz and polarization effects as well as an empirical absorption correction by ψ-scans were applied to the data. The structure was solved by direct methods and subsequent Fourier summations, the least-squares refinement on F converged to $R = 4.6\%$. Details of the structure refinement and a summary of crystal data are given in Table 1, final atomic coordinates and equivalent displacement parameters are listed in Table 2. Tables of observed and calculated structure factors and anisotropic displacement parameters

TABLE 1

Summary of Crystal Data, X-Ray Measurements and Structure Refinement of CoSeO$_3$-II

Space group	$C2/c$ (No. 15)
a [Å]	15.646(3)
b [Å]	9.947(2)
c [Å]	14.984(3)
β [°]	110.65(1)
V [Å^3]	2182.1
Z	32
ρ_{Calc} [g cm^{-3}]	4.527
μ (MoKα) [cm^{-1}]	188.5
Crystal dimensions [mm]	0.4 × 0.2 × 0.2
Crystallographic forms	{110}, {100}, {212}, {$\bar{1}$11}
Extinction coefficient g (19)	6.0(3) × 10^{-7}
Measured reflections	6574
Unique data set	3178
Data with $F_0 > 3\sigma(F_0)$	2948
Variables	182
Transmission factors (ψ-scans)	0.03–0.07
R	0.046
$R_w(w = 1/[\sigma(F_0)]^2)$	0.038

are available from the author. All calculations were done with the program system STRUCSY (14).

RESULTS AND DISCUSSION

In CoSeO$_3$-II the Co(II) atoms are coordinated to oxygen atoms in moderate to strongly distorted octahedral

TABLE 2

Atomic Coordinates and Equivalent Displacement Parameters [pm^2] in CoSeO$_3$-II

	x	y	z	U_{eq}
Co(1)	0.06855(4)	0.11789(6)	0.03275(5)	158
Co(2)	0.26104(4)	0.37146(6)	0.09364(5)	183
Co(3)	0.23221(4)	0.35660(6)	0.41779(5)	168
Co(4)	0.22561(4)	0.09784(6)	0.24112(4)	167
Se(1)	0.37582(3)	0.13721(5)	0.10213(3)	170
Se(2)	0.08396(3)	0.11809(4)	0.36400(3)	154
Se(3)	0.38491(3)	0.32416(4)	0.34925(3)	164
Se(4)	0.09541(3)	0.38468(4)	0.18219(3)	161
O(1)	0.3450(2)	0.2652(3)	0.0196(2)	207
O(2)	0.3077(2)	0.0219(3)	0.0266(2)	212
O(3)	0.3098(2)	0.1914(3)	0.1643(2)	211
O(4)	0.1692(2)	0.1957(3)	0.4527(2)	196
O(5)	0.0321(2)	0.0184(3)	0.4220(2)	186
O(6)	0.1448(2)	0.0060(3)	0.3242(2)	195
O(7)	0.4622(2)	0.2655(3)	0.4491(2)	210
O(8)	0.2898(2)	0.2337(3)	0.3427(2)	183
O(9)	0.3386(2)	0.4725(3)	0.3794(2)	163
O(10)	0.1123(2)	0.3962(3)	0.2987(2)	213
O(11)	0.1131(2)	0.2188(3)	0.1643(2)	183
O(12)	0.1960(2)	0.4459(3)	0.1792(2)	208

Note: $U_{eq} = \frac{1}{3}[U_{22} + 1/\sin^2\beta(U_{11} + U_{33} + 2U_{13}\cos\beta)]$ (20).

arrangements. The Se(IV) atoms are one-sided pyramidally coordinated to three O atoms, a typical configuration indicating the activity of lone-pair electrons of the Se(IV) atoms. All atoms occupy general positions. Interatomic distances and bond angles for the four different CoO$_6$ polyhedra and SeO$_3$ groups in CoSeO$_3$-II as well as octahedral distortion parameters Δ_{oct} and σ^2_{oct} are compiled in Table 3, bond valence calculations according to (15) are summarized in Table 4.

The crystal structure of CoSeO$_3$-II is built up from complex $\frac{2}{\infty}$[Co$_3$(SeO$_3$)$_4$] sheets parallel to (100) (Fig. 1). Paying special attention to polyhedral edge connections, rods composed of two Se(1)O$_3$ pyramids and two Co(2)O$_6$ and Co(4)O$_6$ octahedra as well as smaller groups consisting of two Se(3)O$_3$ and two Co(3)O$_6$ polyhedra can be described. The polyhedral arrangement within the rods is especially worth mentioning; both Se(1)O$_3$ groups occupy the notches located between edge-connected Co(2)O$_6$ octahedra and thus share two of their edges with these octahedra. These Co(2)$_2$Co(4)$_2$Se(1)$_2$O$_{18}$ rods are linked with the smaller Co(3)$_2$Se(3)$_2$O$_{12}$ groups by common corners and by the remaining selenite pyramids of Se(2) and Se(4). The closely packed $\frac{2}{\infty}$[Co$_3$(SeO$_3$)$_4$] sheets are only connected via Co(1)$_2$O$_{10}$ dimers by sharing corners as well as two edges with Co(4)O$_6$ polyhedra in neighboring sheets (Fig. 2). This arrangement results in a network with intersecting channels parallel to b and c, which are obviously occupied by the lone-pair electrons of the Se(IV) atoms.

The polyhedral connections outlined above considerably contribute to bond length and angle distortions of the coordination polyhedra in CoSeO$_3$-II (Table 3). Within the Co(2)$_2$Co(4)$_2$Se(1)$_2$O$_{18}$ rods, the lengths of common edges between Co(2)O$_6$ and Se(1)O$_3$ polyhedra [O(1)–O(2), O(1)–O(3)] as well as between Co(2)O$_6$ and Co(4)O$_6$ octahedra [O(6)–O(12)] and their corresponding bond angles are strongly reduced from "normal" values. The repulsion between the rather closely approaching Se(1) and Co(2) atoms [Se(1)–Co(2) = 2.917(1) and 2.961(1) Å] leads to a marked lengthening of both Co(2)–O(1) distances and to very high values of the distortion parameters Δ_{oct} and σ^2_{oct} for the Co(2)O$_6$ polyhedron. CoO$_6$ octahedra with comparable magnitudes of these distortion parameters are only very rarely found in inorganic crystal structures (compare (16)). Above-average Δ_{oct} values are also observed for the Co(4)O$_6$ octahedron, which is elongated along its O(3)–O(6) axis, and, within the Co(3)$_2$Se(3)$_2$O$_{12}$ groups, for the Co(3)O$_6$ polyhedron. Furthermore, short contacts between Se(3) and Co(3) [Se(3)–Co(3) = 2.932(1) Å] and the strong distortion of the Se(3)O$_3$ pyramid, sharing a very short edge [O(8)–O(9)] with the Co(3)O$_6$ octahedron, are worth noting. As mentioned above, the Se(2)O$_3$ and Se(4)O$_3$ pyramids act as a further linkage between the structural units; for these polyhedra a slight flattening compared to average data from the literature (17) is observed.

Co(1)	O(1)	O(5)	O(5)	O(7)	O(9)	O(11)
O(1)	**2.131(3)**		3.102(5)	2.884(5)	3.329(5)	3.053(5)
O(5)	172.8(3)	**2.161(3)**	2.875(7)	2.871(5)	2.901(4)	2.955(5)
O(5)	95.4(1)	85.8(2)	**2.062(3)**	2.829(5)	2.952(5)	
O(7)	87.1(1)	85.8(1)	86.9(1)	**2.054(3)**		3.261(5)
O(9)	102.3(1)	84.8(1)	89.2(1)	170.1(3)	**2.142(3)**	2.712(4)
O(11)	92.4(1)	87.8(1)	167.4(3)	103.4(1)	79.5(1)	**2.101(3)**

$\langle$Co(1)–O$\rangle$ = 2.109; $\langle$O–O$\rangle$ = 2.977; Δ_{oct} = 0.00036, σ^2_{oct} = 51.3

Co(2)	O(1)	O(1)	O(2)	O(3)	O(6)	O(12)
O(1)	**2.260(3)**	2.837(6)	3.083(5)	2.528(5)	3.313(5)	
O(1)	76.1(2)	**2.344(3)**	2.500(5)	2.989(5)		3.513(5)
O(2)	91.5(1)	69.2(1)	**2.039(3)**		3.211(5)	3.080(5)
O(3)	71.0(1)	84.7(1)	151.7(2)	**2.084(3)**	3.200(5)	3.148(5)
O(6)	100.4(1)	171.6(3)	103.6(1)	101.5(1)	**2.048(3)**	2.579(5)
O(12)	170.3(3)	106.4(1)	98.2(1)	99.7(1)	78.3(1)	**2.036(3)**

$\langle$Co(2)–O$\rangle$ = 2.135; $\langle$O–O$\rangle$ = 2.998; Δ_{oct} = 0.00324, σ^2_{oct} = 182.8

Co(3)	O(2)	O(4)	O(4)	O(8)	O(9)	O(10)
O(2)	**2.039(3)**	3.268(5)	2.986(5)		3.120(5)	2.770(5)
O(4)	106.4(1)	**2.043(3)**	2.654(7)	2.935(5)		2.940(5)
O(4)	93.1(1)	80.3(2)	**2.075(3)**	2.986(5)	3.059(5)	
O(8)	162.4(2)	91.1(1)	92.2(1)	**2.070(3)**	2.496(4)	3.077(5)
O(9)	93.0(1)	158.5(2)	89.7(1)	70.3(1)	**2.259(3)**	3.398(5)
O(10)	83.5(1)	89.8(1)	168.2(3)	94.5(1)	101.7(1)	**2.120(3)**

$\langle$Co(3)–O$\rangle$ = 2.101; $\langle$O–O$\rangle$ = 2.974; Δ_{oct} = 0.00129, σ^2_{oct} = 88.9

Co(4)	O(3)	O(6)	O(8)	O(9)	O(11)	O(12)
O(3)	**2.235(3)**		2.831(5)	3.079(5)	3.090(5)	3.408(5)
O(6)	177.7(3)	**2.257(3)**	3.148(5)	3.170(5)	3.103(5)	2.579(5)
O(8)	83.3(1)	94.7(1)	**2.018(3)**		3.098(5)	2.899(5)
O(9)	89.7(1)	92.4(1)	172.3(3)	**2.132(3)**	2.712(4)	3.053(5)
O(11)	90.7(1)	90.6(1)	97.3(1)	79.5(1)	**2.108(3)**	
O(12)	105.5(1)	73.5(1)	91.0(1)	94.0(1)	162.6(2)	**2.044(3)**

$\langle$Co(4)–O$\rangle$ = 2.132; $\langle$O–O$\rangle$ = 3.014; Δ_{oct} = 0.00174, σ^2_{oct} = 69.7

Se(1)	O(1)	O(2)	O(3)
O(1)	**1.721(3)**	2.500(5)	2.528(5)
O(2)	94.0(2)	**1.698(3)**	2.655(5)
O(3)	95.1(2)	102.6(2)	**1.704(3)**

$\langle$Se(1)–O$\rangle$ = 1.708; $\langle$O–Se(1)–O$\rangle$ = 97.2

Se(2)	O(4)	O(5)	O(6)
O(4)	**1.700(3)**	2.688(5)	2.626(5)
O(5)	104.5(2)	**1.701(3)**	2.663(5)
O(6)	100.9(2)	102.9(2)	**1.705(3)**

$\langle$Se(2)–O$\rangle$ = 1.702; $\langle$O–Se(2)–O$\rangle$ = 102.8

Se(3)	O(7)	O(8)	O(9)
O(7)	**1.662(3)**	2.623(5)	2.765(5)
O(8)	102.0(2)	**1.712(3)**	· 1.496(4)
O(9)	107.2(2)	91.5(2)	**1.771(3)**

$\langle$Se(3)–O$\rangle$ = 1.715; $\langle$O–Se(3)–O$\rangle$ = 100.2

Se(4)	O(10)	O(11)	O(12)
O(10)	**1.675(3)**	2.680(5)	2.612(5)
O(11)	104.7(2)	**1.709(3)**	2.575(5)
O(12)	101.3(2)	98.0(2)	**1.703(3)**

$\langle$Se(4)–O$\rangle$ = 1.696; $\langle$O–Se(4)–O$\rangle$ = 101.3

TABLE 4
Bond Valence Calculations According to (15) for CoSeO₃-II

ν[vu]	Co(1)	Co(2)	Co(3)	Co(4)	Se(1)	Se(2)	Se(3)	Se(4)	Σ
O(1)	0.31	0.22 + 0.17			1.28				1.98
O(2)		0.39	0.39		1.36				2.14
O(3)		0.35		0.23	1.34				1.92
O(4)			0.39 + 0.36			1.35			2.10
O(5)	0.28 + 0.37					1.35			2.00
O(6)		0.38		0.22		1.33			1.93
O(7)	0.38						1.50		1.88
O(8)			0.36	0.41			1.31		2.08
O(9)	0.30		0.22	0.30			1.11		1.93
O(10)			0.31					1.44	1.75
O(11)	0.33			0.32				1.32	1.97
O(12)		0.39		0.39				1.34	2.12
Σ	1.97	1.90	2.03	1.87	3.98	4.03	3.92	4.10	

Despite the strong distortion of most of the coordination polyhedra in CoSeO₃-II, the observed mean bond lengths generally comply well with crystal chemical expectations (16, 17).

Except for O(1), O(7), O(9), and O(10), the oxygen atoms in CoSeO₃-II are coordinated to three cations in slightly pyramidal to planar arrangements. Corresponding bond angle sums range from 340.7° to 360.0°. Out of the remaining oxygen atoms, O(7) and O(10) are only coordinated to one Se and one Co atom with bonds angles of 121.8° and 129.2°, respectively, while O(1) and O(9) have a distorted tetrahedral environment of one Se and three Co

atoms each. Bond valence sums calculated for the oxygen atoms and for the cations in CoSeO₃-II (Table 4) are in a range that is usual for the respective elements. The largest deviation from the ideal values is observed for the twofold coordinated O(10) atom with 1.75 vu. For this oxygen a small additional contribution (0.07 vu) to its bond valence sum from a comparatively close Se(1) atom in the second coordination sphere may be assumed [Se(1)–O(10) = 2.792(3) Å].

The structure of CoSeO₃-II is closely related to that of $Co_3(SeO_3)_3 \cdot H_2O$ (6) [and the isotypic compound $Ni_3(SeO_3)_3 \cdot H_2O$ (6, 18)]. $Co_3(SeO_3)_3 \cdot H_2O$ is build up
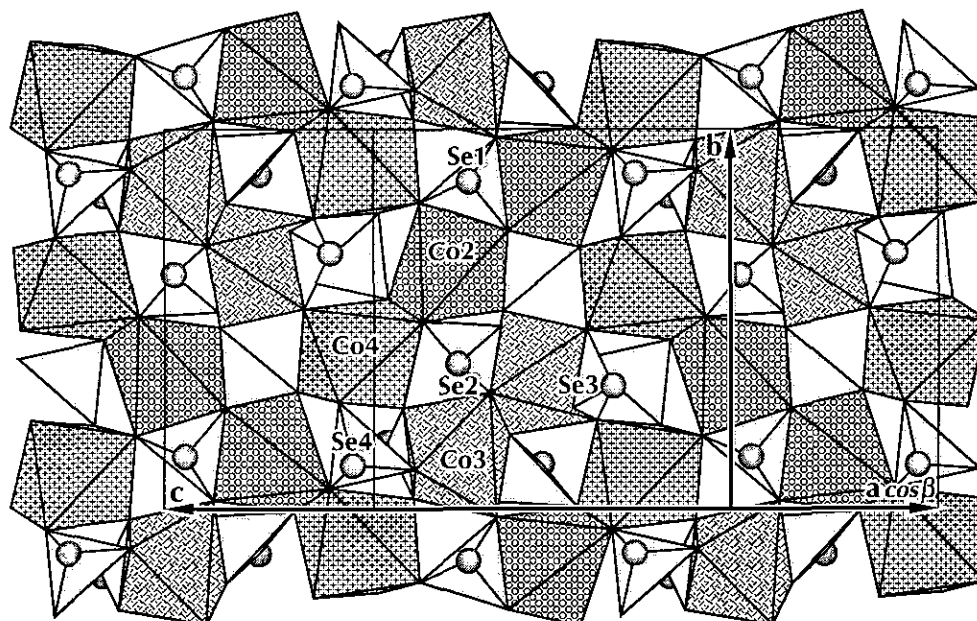
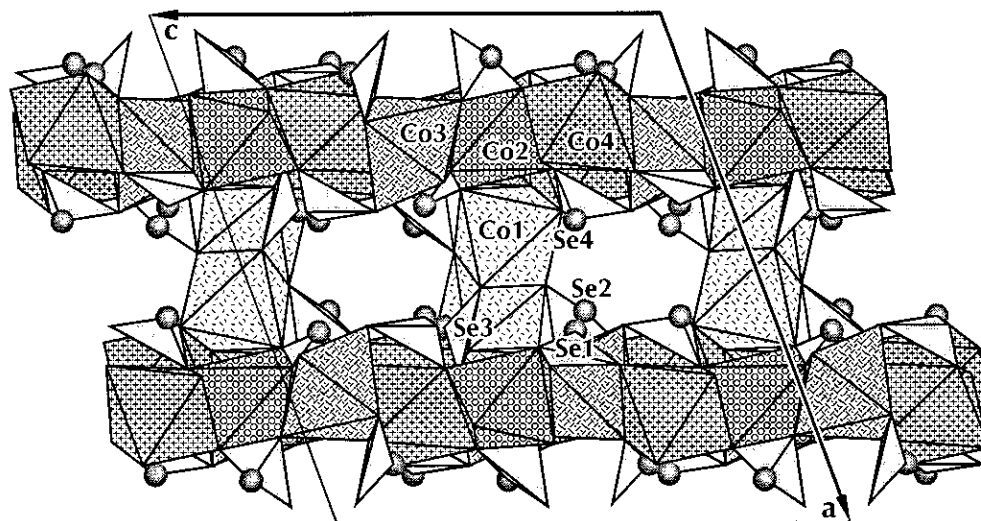FIG. 1. Projection of the crystal structure of CoSeO₃-II on (100), showing a $_\infty^2[Co_3(SeO_3)_4]$ sheet.

FIG. 2. Projection of the crystal structure of CoSeO₃-II on (010).

from $\overset{2}{\infty}[\text{Co}_5(\text{SeO}_3)_6 \cdot 2\text{H}_2\text{O}]$ sheets which contain similar structural units as found in the title compound; in Co₃ (SeO₃)₃ · H₂O the above-mentioned "rods" are connected to infinite chains which are further linked by smaller groups composed of two SeO₃ and two CoO₆ polyhedra [compare Fig. 1 in (6)]. The unusual position of selenite pyramids within the notches between edge-sharing CoO₆ octahedra is topologically identical with the situation in CoSeO₃-II and leads to a comparable extent of polyhedral distortion. These sheets are tied together by single CoO₆ octahedra, thereby, in analogy with CoSeO₃-II, forming a system of intersecting channels, occupied by lone-pair electrons of the Se(IV) atoms [compare Fig. 2 in (6)].

The high-pressure modification of CoSeO₃, investigated by Kohn et al. (1), forms a completely different structure, which can be derived from the perovskite structure type; CoO₆ octahedra are linked by common corners to a three-dimensional network; the SeO₃ groups, located in the cavities of this network, also share corners with three CoO₆ octahedra, thus leading to polyhedral distortions and a strong deviation from an ideal perovskite-type structure. As expected, the high-pressure modification of CoSeO₃ has a much closer average polyhedral packing $(\rho_{\text{calc}} = 5.45 \text{ g cm}^{-3})$ compared to the title compound $(\rho_{\text{calc}} = 4.53 \text{ g cm}^{-3})$, whereas the reported (1) mean interatomic distances (<Co–O> = 2.143 Å, <Se–O> = 1.717 Å) are longer than found in CoSeO₃-II and are also significantly above corresponding average values given in the literature (16, 17).

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