Preparation and crystal structure investigation of $Sr_2Co(SeO_3)_3$

Manfred Wildner

Institut für Mineralogie und Kristallographie der Universität Wien, Dr. Karl Lueger-Ring 1, A-1010 Vienna, Austria

Abstract

The structure of hydrothermally synthesized $Sr_2Co(SeO_3)_3$ was determined using single-crystal X-ray diffraction data up to $\sin \theta/\lambda = 0.81$ Å^{-1} (triclinic; space group, $P\bar{1}$; $a = 7.326(2)$ Å, $b = 7.605(2)$ Å, $c = 8.734(2)$ Å, $\alpha = 103.19(1)°$, $\beta = 105.50(1)°$, $\gamma = 95.52(1)°$; $Z = 2$; $R_w = 0.032$ for 2973 unique reflections with $F_o > 3\sigma(F_o)$). $Sr_2Co(SeO_3)_3$ forms a three-dimensional network structure composed of SrO_8, CoO_6, and SeO_3 polyhedra. Sr–O distances range from 2.513 to 2.846 Å (Sr1) and from 2.530 to 2.991 Å (Sr2), and Co–O distances from 2.048 to 2.256 Å; Se–O bond lengths within three crystallographically different selenite groups were determined between 1.666 and 1.715 Å. $Sr_2Co(SeO_3)_3$ is isotypic with the corresponding copper compound, although in $Sr_2Cu(SeO_3)_3$ the environment of the Cu(II) atoms is strongly Jahn–Teller distorted to a tetragonal pyramidal [4+1] coordination with only weak interaction to a sixth oxygen ligand.

Keywords: Crystal structure; Crystal chemistry; Jahn–Teller effect

1. Introduction

Recently, single crystals of $Sr_2Co(SeO_3)_3$ could be prepared under low hydrothermal conditions. An investigation of the crystal structure of this new compound seemed to be of interest for several reasons; on one hand, $Sr_2Co(SeO_3)_3$ is the first crystalline representative in the system of alkaline earth cobalt(II) selenites; on the other hand, preliminary X-ray investigations indicated that $Sr_2Co(SeO_3)_3$ is isotypic with the corresponding copper(II) compound, $Sr_2Cu(SeO_3)_3$, which was structurally characterized by Effenberger [1]. Because of differences in the d electron configurations of Co(II) and Cu(II) isotypic compounds of these two transition metal elements are rare: the d^9 configuration of Cu(II) ions gives rise to strong Jahn–Teller distortions of Cu^{II}O$_6$ polyhedra [2–5], whereas the d^7 configuration of Co(II) ions apparently does not induce any significant distortion of Co^{II}O$_6$ octahedra [6]. Among selenites, for example, isotypic cobalt and copper compounds are known so far only in the Me^{II}(SeO$_3$)-I structure type [7] (type notation according to Ref. [8]) and in the Me^{II}(SeO$_3$)·2H$_2$O (cobaltomenite-) structure type [9,10]. As a new example, in the present paper we report the synthesis and crystal structure of the cobalt analogue of $Sr_2Cu(SeO_3)_3$ [1], thus also continuing a study on crystal structures and crystal chemistry of Co(II) selenites [10–15].

2. Experimental

For the hydrothermal preparation of $Sr_2Co(SeO_3)_3$ an appropriate mixture of Sr(OH)$_2$, Co(OH)$_2$, SeO$_2$ and some drops of water were inserted in a Teflon-lined steel vessel (capacity, about 6 ml; filling degree, about 20%) and kept at about 493 K for 32 h. As a result, violet single crystals of $Sr_2Co(SeO_3)_3$ up to about 0.8 mm with crystallographic forms {100}, {010}, and {001} were obtained. Preliminary X-ray investigations by oscillation and Weissenberg photographs indicated that $Sr_2Co(SeO_3)_3$ is isotypic with $Sr_2Cu(SeO_3)_3$ [1]. Lattice parameters (refined from 44 accurate 2θ values in the range $36° < 2\theta < 42°$) and X-ray diffraction intensities up to $2\theta = 70°$ were measured on a Stoe four-circle diffractometer (AED2) with graphite-monochromatized Mo Kα radiation (2θ–ω scans; 35 steps per reflection, increased for α_1–α_2 splitting; 0.03° and 0.5–1.5 s step^{-1}; 2×5 steps for background measurements; three standard reflections each 120 min). An empirical correction for absorption effects (Ψ scan data) and corrections for Lorentz and polarization effects were applied. Complex scattering curves from Ref. [16] were used. The full-matrix least-squares refinement on F was started with the atomic coordinates for $Sr_2Cu(SeO_3)_3$ [1]. Subsequently, anisotropic displacement parameters and a secondary isotropic extinction factor [17] were included, giving a total of 137 param-

Table 1
Summary of crystal data, X-ray measurements and structure refinement of $Sr_2Co(SeO_3)_3$

Space group	$P\bar{1}$ (no. 2)
a (Å)	7.326(2)
b (Å)	7.605(2)
c (Å)	8.734(2)
α (deg)	103.19(1)
β (deg)	105.50(1)
γ (deg)	95.52(1)
V (Å³)	450.1
Z	2
ρ_{calc} (g cm^{-3})	4.539
μ(Mo Kα) (cm^{-1})	252.8
Crystal dimensions (mm × mm × mm)	0.09 × 0.11 × 0.25
Extinction coefficient g	1.99(4) × 10^{-5}
Measured reflections	7953
Unique data set	3976
Data with $F_o > 3\sigma(F_o)$	2973
Variables	137
Transmission factors (ψ scans)	0.02–0.09
R	0.054
R_w ($w = 1/[\sigma(F_o)]^2$)	0.032

eters. Table 1 lists further details of the structure refinement and a summary of crystal data. The final atomic coordinates and anisotropic displacement parameters are given in Table 2. All calculations were done with the program system STRUCSY [18].

3. Results and discussion

Important interatomic distances and bond angles in $Sr_2Co(SeO_3)_3$ are listed in Table 3. Fig. 1 shows the crystal structure in a projection along [100]. Main

structural units are two crystallographically different SrO_8 polyhedra, one type of CoO_6 octahedra, and three types of pyramidal SeO_3 groups. All atoms in $Sr_2Co(SeO_3)_3$ occupy general sites with symmetry 1.

Individual and mean Sr1–O and Sr2–O distances (Table 3) are in the range expected for SrO_8 polyhedra, judging for example from the effective ionic radius for Sr[8] cited in the literature [19], or from bond valence calculations according to Ref. [20] giving bond valence sums of 1.96 and 1.98 valence units (VUs) for Sr1 and Sr2 respectively. For both Sr atoms further Sr–O distances exceed 3.33 Å. The Sr atoms are linked by common O–O edges forming chains of Sr(1)O$_8$ polyhedra (common edges: O11–O11, 3.275(7) Å; O12–O12, 2.814(7) Å) and pairs of Sr(2)O$_8$ polyhedra (common edge: O13–O13, 3.247(6) Å), which are further linked by common edges (O11–O32, 3.255(5) Å; O21–O31, 2.868(5) Å) to a three-dimensional framework.

The Co atoms occupy distorted octahedral sites within this framework. The mean Co–O distance is close to the average value for Co(II)[6]–O bonds [6]; bond valence calculations [20] give 1.92 VUs. The magnitudes of the bond length distortion $\Delta_{oct} = 0.001\ 08$ ($\Delta_{oct} = (1/6)\Sigma [(d_i - d_m)/d_m]^2$) and especially of the bond angle distortion $\sigma_{oct}^2 = 116.0$ ($\sigma_{oct}^2 = (1/11)\Sigma (a_i - 90°)^2$) are rather high, but CoO_6 octahedra with similar or higher distortion parameters are occasionally found in inorganic compounds [6]. The CoO_6 polyhedra are not connected with each other but share four edges with SrO_8 polyhedra and the shortest edge with the Se(1)O$_3$ group (Table 3). This linkage also contributes significantly to the bond angle distortion of the CoO_6 polyhedron.

The characteristic pyramidal shape of the SeO_3 groups is caused by the activity of lone pair electrons of the Se(IV) atoms. Mean Se–O bond lengths and angles

Table 2
Atomic coordinates and anisotropic displacement parameters (picometres squared) in $Sr_2Co(SeO_3)_3$ (with estimated standard deviations in parentheses)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sr1	0.245 39(6)	0.088 33(5)	0.389 84(5)	185(2)	149(2)	154(3)	33(1)	40(2)	26(2)
Sr2	0.370 42(6)	0.517 48(5)	0.192 71(6)	211(2)	146(2)	189(3)	16(1)	56(2)	38(2)
Co	0.907 28(9)	0.663 88(8)	0.247 39(8)	167(3)	137(2)	182(4)	23(2)	50(2)	34(2)
Se1	0.636 92(6)	0.917 20(5)	0.203 54(6)	184(2)	126(2)	181(3)	35(1)	57(2)	39(2)
Se2	0.901 47(6)	0.209 29(5)	0.042 89(6)	163(2)	119(2)	172(3)	23(1)	48(2)	31(2)
Se3	0.762 50(6)	0.363 64(6)	0.411 94(6)	178(2)	124(2)	176(3)	31(1)	44(2)	35(2)
O11	0.490 5(5)	0.877 7(4)	0.316 7(4)	214(16)	180(13)	265(19)	57(12)	122(14)	44(13)
O12	0.855 2(4)	0.949 2(4)	0.347 5(4)	151(15)	209(14)	192(18)	−10(11)	−1(13)	36(13)
O13	0.633 0(4)	0.698 3(4)	0.097 6(4)	178(15)	165(13)	205(19)	29(11)	64(13)	−7(13)
O21	1.124 7(5)	0.247 4(4)	0.169 3(4)	175(16)	195(14)	262(20)	−2(12)	−11(14)	69(14)
O22	0.832 8(5)	0.417 6(4)	0.072 4(4)	294(19)	189(15)	242(20)	135(14)	17(15)	−6(14)
O23	0.932 0(5)	0.184 6(5)	−0.144 5(4)	248(17)	263(16)	124(18)	−40(13)	53(14)	22(14)
O31	0.523 1(5)	0.298 7(5)	0.351 9(5)	197(17)	261(17)	339(22)	−30(13)	−14(15)	147(16)
O32	0.774 4(5)	0.590 6(4)	0.414 4(4)	323(19)	130(13)	288(20)	28(13)	140(16)	39(14)
O33	0.822 4(5)	0.359 9(5)	0.610 9(4)	218(17)	291(17)	169(19)	72(13)	60(14)	82(15)

The anisotropic displacement parameter is defined as $\exp(-2\pi^2 \Sigma_i \Sigma_j U_{ij} h_i h_j a_i^* a_j^*)$.

Table 3

Selected bond lengths, polyhedral edge lengths (ångströms) and bond angles (degrees) as well as relevant mean values (< >) in Sr₂Co(SeO₃)₃ (estimated standard deviations in parentheses)

Co	O22	O23	O33	O32	O13	O12
O22	2.048(3)	3.172(5)	3.194(5)	3.136(5)	2.703(5) [a]	
O23	100.7(1)	2.073(3)	2.752(5)		3.115(5)	2.751(5) [b]
O33	101.2(2)	82.9(1)	2.085(3)	3.015(5)		3.498(5)
O32	98.2(1)	161.1(3)	92.2(1)	2.100(3)	3.011(5) [a]	2.955(5) [b]
O13	79.9(1)	94.7(1)	177.5(4)	89.9(1)	2.161(3)	2.581(5) [c]
O12	151.1(3)	78.8(1)	107.3(1)	85.3(1)	71.5(1)	2.256(3)

<Co–O>, 2.121; <O–O>, 2.990

Se1	O11	O13	O12			
O11	1.690(3)	2.601(5) [a]	2.603(5) [b]	Sr1–O21	2.513(3)	
O13	100.0(2)	1.704(3)	2.581(5) [c]	Sr1–O23	2.560(3)	
O12	100.1(2)	98.4(2)	1.705(3)	Sr1–O31	2.605(3)	
<Se1–O>, 1.700; <O–Se1–O>, 99.5				Sr1–O11	2.627(3)	
				Sr1–O12	2.655(3)	
				Sr1–O32	2.684(3)	
				Sr1–O11	2.707(3)	

Se2	O21	O23	O22			
O21	1.666(3)	2.634(5)	2.651(5)	Sr1–O12	2.846(3)	
O23	103.8(2)	1.682(3)	2.590(5)	<Sr1–O>	2.650	
O22	104.3(2)	100.3(2)	1.693(3)			
<Se2–O>, 1.680; <O–Se2–O>, 102.8				Sr2–O21	2.530(3)	
				Sr2–O31	2.556(3)	
				Sr2–O33	2.574(3)	
				Sr2–O22	2.577(3)	

Se3	O31	O33	O32			
O31	1.679(3)	2.610(5)	2.596(5) [a]	Sr2–O11	2.669(3)	
O33	101.9(2)	1.683(3)	2.705(5)	Sr2–O13	2.674(3)	
O32	99.8(2)	105.6(2)	1.715(3)	Sr2–O13	2.680(3)	
<Se3–O>, 1.692; <O–Se3–O>, 102.4				Sr2–O32	2.991(3)	
				<Sr2–O>	2.656	

[a] Common edge with Sr(2)O₈.
[b] Common edge with Sr(1)O₈.
[c] Edge shared by CoO₆ and Se(1)O₃.

generally agree with data compiled in the literature [21,22]; somewhat short mean Se–O distances and a slight flattening of the Se(2)O₃ and Se(3)O₃ pyramids are, however, significant. Bond valence sums [20] for Se1, Se2, and Se3 are 4.05 VUs, 4.27 VUs, and 4.14 VUs respectively. Linkage of the SeO₃ groups with adjacent SrO₈ or CoO₆ polyhedra is achieved by three common edges (Se1), by sharing one edge and one corner (Se3), or by three common corners only (Se2). The arrangement of the Se(1)O₃ and Se(2)O₃ groups within the crystal structure results in the formation of narrow channels along [100], which are obviously occupied by the lone pair electrons of these selenium atoms (Fig. 1).

The oxygen atoms in Sr₂Co(SeO₃)₃ are coordinated to three cations in nearly planar configurations (O21, O22, O23, O31, O33) or to four cations in strongly distorted tetrahedral arrangements (O11, O12, O13, O32). Calculated bond valence sums [20] range from 1.92 VUs for O12 to 2.15 VUs for O21.

As stated above, Sr₂Co(SeO₃)₃ is isotypic with the copper compound Sr₂Cu(SeO₃)₃ [1]. However, the replacement of Co(II) ions (d⁷ configuration) by

Jahn–Teller distorted Cu(II) ions (d⁹ configuration) leads to striking differences in the structures of these compounds. In Sr₂Cu(SeO₃)₃ the Cu atoms are [4 + 1] coordinated to four approximately coplanar oxygens (O23, O33, O13, O32) with Cu–O distances from 1.969 to 2.022 Å, and a fifth oxygen (O22) with a Cu–O distance 2.188 Å completing the tetragonal pyramidal arrangement, while a further oxygen (O12) follows only at 2.612 Å [1]. As expected, the four short Cu–O bond lengths increase in the cobalt compound, in particular Co–O13, whereas the two longer trans-configured Cu–O22 and Cu–O12 distances are strongly shortened, resulting in a sixfold octahedral environment for the Co atom in Sr₂Co(SeO₃)₃. Both tendencies lead to a more regular shape of the Se(1)O₃ pyramid and, furthermore, to slightly higher bond length distortions of the SrO₈ polyhedra in Sr₂Co(SeO₃)₃ as compared with Sr₂Cu(SeO₃)₃.

Despite the fact that the Sr₂Meᴵᴵ(SeO₃)₃ structure type allows strong distortions of the MeO₆ octahedra with lengthening of two trans-configured Me–O bonds (in Sr₂Cu(SeO₃)₃), the Co(II) atom adopts a clearly differently distorted environment in Sr₂Co(SeO₃)₃. This
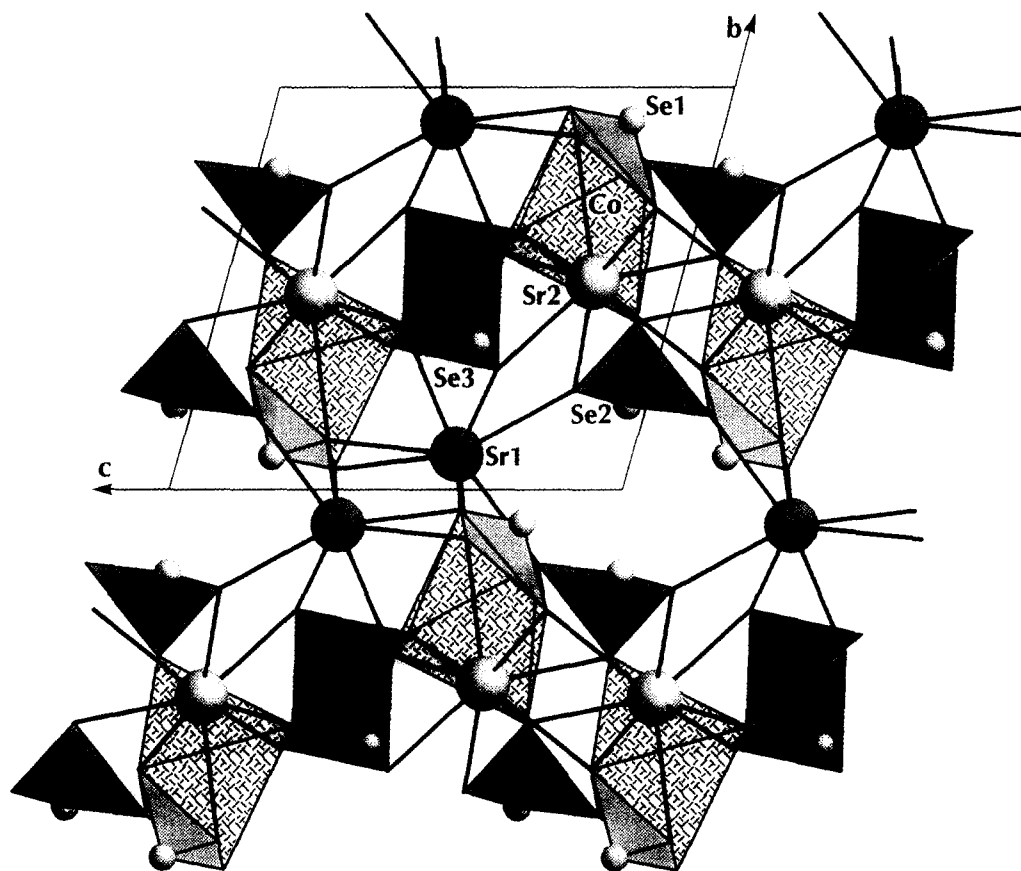
Fig. 1. The crystal structure of $Sr_2Co(SeO_3)_3$ in a projection along [100].

is in agreement with an earlier investigation [6], revealing that Co(II) ions are not preferentially stabilized in elongated octahedral oxygen coordination, although this is predicted by crystal field theory.

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