

Crystal Structures of $\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ and $\text{Ni}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$, Two New Isotypic Compounds

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Summary. The crystal structures of the new, hydrothermally synthesized, isotypic compounds $\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ and $\text{Ni}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ were determined by direct and Fourier methods and refined to $R_w = 0.023, 0.032$ using single crystal X-ray data up to $\sin \theta/\lambda = 0.81 \text{ \AA}^{-1}$ [space group $\text{P}\bar{1}$, $a = 8.102$ (2), 7.986 (3) Å ; $b = 8.219$ (2), 8.133 (3) Å ; $c = 8.572$ (2), 8.422 (3) Å , $\alpha = 69.15$ (1), 69.50 (1)°; $\beta = 62.88$ (1), 62.50 (1)°; $\gamma = 67.23$ (1), 67.64 (1)°; $Z = 2$]. The structures are built up from $[\text{Me}_5(\text{SeO}_3)_6 \cdot 2 \text{H}_2\text{O}]^{2-}$ sheets containing three crystallographically different types of octahedrally coordinated Me^{2+} and trigonal pyramidal coordinated Se^{4+} atoms, respectively. These sheets are linked only by a fourth type of $\text{Me}^{2+[\text{6}]}$ atom. All coordination polyhedra deviate significantly from their ideal shapes, bond lengths within the extremely distorted $\text{Me}(4)\text{O}_6$ polyhedra range from 1.983 (2) Å to 2.403 (2) Å in $\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ and from 1.987 (4) Å to 2.301 (3) Å in the Ni compound, O–Se–O bond angles were found between 92.8 (2)° and 104.9 (1)°. Hydrogen bond lengths are 2.802 (3) Å and 2.600 (4) Å in the Co compound, and 2.762 (6) Å and 2.561 (6) Å in $\text{Ni}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$. The latter is one of the shortest known hydrogen bonds donated by a water molecule.

Keywords. $\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$; $\text{Ni}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$; Crystal structure; Crystal chemistry; Short hydrogen bonds.

Die Kristallstrukturen von $\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ und $\text{Ni}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$, zwei neue isotype Verbindungen

Zusammenfassung. Die Kristallstrukturen der neuen, hydrothermal synthetisierten, isotypen Verbindungen $\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ und $\text{Ni}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ wurden mit direkten und Fourier-Methoden bestimmt und unter Verwendung von Einkristallröntgendaten bis $\sin \theta/\lambda = 0.81 \text{ \AA}^{-1}$ auf R_w -Werte von $0.023, 0.032$ verfeinert [Raumgruppe $\text{P}\bar{1}$, $a = 8.102$ (2), 7.986 (3) Å ; $b = 8.219$ (2), 8.133 (3) Å ; $c = 8.572$ (2), 8.422 (3) Å , $\alpha = 69.15$ (1), 69.50 (1)°; $\beta = 62.88$ (1), 62.50 (1)°; $\gamma = 67.23$ (1), 67.64 (1)°; $Z = 2$]. Die Strukturen werden von $[\text{Me}_5(\text{SeO}_3)_6 \cdot 2 \text{H}_2\text{O}]^{2-}$ Schichten aufgebaut, die je drei kristallographisch unterschiedliche Arten von oktaedrisch koordinierten Me^{2+} und trigonal pyramidal koordinierten Se^{4+} Atomen enthalten. Diese Schichten sind nur durch eine vierte Art von $\text{Me}^{2+[\text{6}]}$ Atomen verknüpft. Alle Koordinationspolyeder weichen deutlich von ihren Idealformen ab, Bindungslängen in den extrem verzerrten $\text{Me}(4)\text{O}_6$ Polyedern variieren zwischen 1.983 (2) Å und 2.403 (2) Å in $\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ und zwischen 1.987 (4) Å und 2.301 (3) Å in der Ni-Verbindung, O–Se–O-Bindungswinkel liegen zwischen 92.8 (2)° und 104.9 (1)°. Wasserstoffbrückenlängen sind 2.802 (3) Å und 2.600 (4) Å in der Co-Verbindung, und 2.762 (6) Å und 2.561 (6) Å in $\text{Ni}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$. Letztere ist eine der kürzesten bekannten Wasserstoffbrücken eines Wassermoleküls.

Introduction

In the course of the author's investigations of Co^{2+} and Ni^{2+} selenites, the crystal structures of $\text{NaCo}_2(\text{SeO}_3)_2(\text{OH})$ [1, 2] and of $\text{CoSeO}_3 \cdot 2 \text{H}_2\text{O}$ and $\text{NiSeO}_3 \cdot 2 \text{H}_2\text{O}$

[3] were determined or refined previously. Recently, single crystals of $\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ were obtained by hydrothermal synthesis. The determined crystal structure showed some remarkable features: strongly distorted coordination polyhedra and a very short hydrogen bond. It seemed interesting to compare this structure to an isotopic compound containing a Me^{2+} ion that (1) prefers a more regular octahedral coordination and (2) is smaller than the Co^{2+} ion. Therefore attempts were made to obtain the isotopic Ni compound, $\text{Ni}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$.

Experimental

Crystals of the title compounds were synthesized under hydrothermal conditions. Teflon lined steel vessels ($V \approx 4 \text{ cm}^3$) were filled with $\approx 0.5 \text{ g}$ of approximately equimolar amounts of $\text{Co}(\text{OH})_2$, KHCO_3 and H_2SeO_4 . NiO, SeO_2 and a NaOH pellet were used for the preparation of the Ni compound. In both cases a few drops of water were added. The closed vessels were heated to $\approx 210^\circ\text{C}$ and kept at this temperature for five days. Dark violet, pleochroic crystals of $\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ up to $\approx 0.3 \text{ mm}$ and yellow crystals of $\text{Ni}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ up to $\approx 0.2 \text{ mm}$ were obtained. Predominant forms of the platelike crystals are $\{001\}$ (Co) and $\{011\}$ (Ni).

Table 1. Cell parameters of $\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ and $\text{Ni}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ and details of X-ray data collections and structure refinements

Compound	$\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$	$\text{Ni}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$
Space group	$\text{P}\bar{1}$	$\text{P}\bar{1}$
a [\AA]	8.102 (2)	7.986 (3)
b [\AA]	8.219 (2)	8.133 (3)
c [\AA]	8.572 (2)	8.422 (3)
α [$^\circ$]	69.15 (1)	69.50 (1)
β [$^\circ$]	62.88 (1)	62.50 (1)
γ [$^\circ$]	67.23 (1)	67.64 (1)
V [\AA^3]	457.10	438.41
Formula units per cell	2	2
Calculated density ρ_{calc} [g cm^{-3}]	4.18	4.36
Absorption coefficient $\mu(\text{MoK}\alpha)$ [cm^{-1}]	168.86	183.60
Equipment	Stoe four circle diffractometer AED2; graphite monochromatized MoK α -radiation; program system STRUCSY (Stoe & Cie, Darmstadt, FRG)	
Data collection	2 θ - ω scans; 45, 48 steps/reflection, increased for $\alpha_1 - \alpha_2$ splitting; 0.03° and $0.5 - 1.5 \text{ s}$ /step; 2^*7 , 8 steps for background measurements; 3, 4 standard reflections each 120 min; $2\theta_{\text{max}} = 70.0^\circ$	
Crystal dimensions [mm]	$0.18 \times 0.10 \times 0.04$	$0.15 \times 0.10 \times 0.05$
Extinction coefficient g [5]	$1.70 (7) \cdot 10^{-5}$	$0.31 (5) \cdot 10^{-5}$
Total measured reflections	8 256	8 178
Unique data set	4 043	3 869
Reflections with $F_0 > 3\sigma(F_0)$ (refinement)	3 272	2 879
Absorption correction	numerical	ψ -scans
min/max Transmission factors	0.16/0.52	0.07/0.20
Number of variables	157	152
Reliability index R	0.032	0.045
R_w ($w = 1/[\sigma(F_0)]^2$)	0.023	0.032
Goodness of fit	1.65	1.95

Table 2. Structure parameters of $\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ and $\text{Ni}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ with e.s.d.'s in parentheses. Given U_{ij} are multiplied by 10^4 (* fixed in the final refinement).
 $ATF = \exp[-2\pi^2 \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} a_i^* a_j^* h_i h_j]$

Atom	x/a	y/b	z/c	U_{11}/U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$									
Co1	0	0	0	116 (2)	146 (2)	134 (3)	-42 (2)	-44 (2)	-15 (2)
Co2	1/2	1/2	1/2	141 (2)	118 (2)	150 (3)	-44 (2)	-58 (2)	-25 (2)
Co3	0.65388 (5)	0.03726 (5)	0.79895 (6)	134 (2)	149 (2)	153 (2)	-45 (1)	-53 (2)	-30 (2)
Co4	0.71664 (5)	0.85636 (5)	0.39005 (6)	135 (2)	151 (2)	162 (2)	-52 (1)	-51 (2)	-16 (2)
Se1	0.56457 (4)	0.23365 (4)	0.23877 (4)	130 (1)	127 (1)	141 (1)	-35 (1)	-46 (1)	-23 (1)
Se2	0.79662 (4)	0.66737 (4)	0.06492 (4)	125 (1)	121 (1)	141 (1)	-29 (1)	-36 (1)	-31 (1)
Se3	0.17624 (4)	0.66966 (4)	0.29811 (4)	133 (1)	129 (1)	156 (1)	-36 (1)	-53 (1)	-30 (1)
O1	0.3023 (3)	0.7124 (3)	0.3858 (3)	167 (9)	171 (10)	165 (11)	-59 (8)	-80 (8)	-15 (8)
O2	0.5468 (3)	0.6953 (3)	0.5643 (3)	174 (9)	162 (10)	163 (11)	-68 (8)	-23 (8)	-70 (8)
O3	0.2128 (3)	0.8964 (3)	0.7589 (3)	123 (9)	185 (10)	194 (11)	-23 (7)	-66 (8)	-54 (9)
O4	0.5375 (3)	0.9447 (3)	0.6739 (3)	175 (9)	163 (10)	174 (11)	-75 (8)	-80 (8)	-23 (8)
O5	0.9496 (3)	0.7241 (3)	0.4515 (3)	137 (9)	275 (12)	143 (10)	-58 (8)	-42 (8)	-32 (9)
O6	0.7083 (3)	0.5180 (3)	0.2467 (3)	193 (10)	144 (10)	201 (12)	-72 (8)	-17 (9)	-5 (9)
O7	0.5988 (3)	0.8268 (3)	0.0273 (3)	120 (9)	171 (10)	181 (11)	-4 (7)	-56 (8)	-21 (9)
O8	0.8667 (3)	0.7852 (3)	0.1424 (3)	191 (10)	204 (10)	165 (11)	-105 (8)	-53 (9)	-38 (9)
O9	0.1894 (3)	0.8592 (3)	0.1263 (3)	152 (9)	176 (10)	154 (11)	-68 (8)	-58 (8)	6 (8)
Ow	0.9179 (3)	0.8725 (4)	0.6893 (4)	158 (11)	328 (14)	262 (14)	-35 (9)	-56 (10)	-180 (11)
H1	1.004 (6)	0.867 (6)	0.704 (6)	312 (117)					
H2	0.935 (5)	0.823 (5)	0.624 (5)	79 (86)					

Table 2 (continued)

Atom	x/a	y/b	z/c	U_{11}/U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$Ni_3(SeO_3)_3 \cdot H_2O$									
Ni1	0	0	0	148 (4)	154 (4)	151 (4)	-39 (3)	-62 (3)	-27 (3)
Ni2	1/2	1/2	1/2	167 (5)	138 (4)	160 (4)	-35 (3)	-72 (3)	-35 (3)
Ni3	0.65333 (10)	0.03803 (9)	0.80011 (9)	179 (3)	182 (3)	183 (3)	-39 (3)	-70 (2)	-49 (2)
Ni4	0.71104 (10)	0.86555 (8)	0.38953 (8)	162 (3)	159 (3)	171 (3)	-43 (2)	-64 (2)	-27 (2)
Se1	0.56618 (7)	0.23663 (6)	0.23661 (6)	153 (2)	149 (2)	157 (2)	-29 (2)	-60 (2)	-31 (2)
Se2	0.79828 (8)	0.66967 (7)	0.06025 (6)	176 (3)	158 (2)	169 (2)	-37 (2)	-62 (2)	-39 (2)
Se3	0.17593 (7)	0.66932 (6)	0.29727 (7)	163 (3)	152 (2)	179 (2)	-27 (2)	-79 (2)	-36 (2)
O1	0.3020 (5)	0.7121 (5)	0.3890 (5)	179 (19)	208 (16)	208 (16)	-49 (14)	-110 (14)	-26 (13)
O2	0.5504 (5)	0.6903 (4)	0.5616 (4)	214 (19)	142 (15)	162 (15)	-56 (14)	-49 (13)	-61 (12)
O3	0.2082 (5)	0.8946 (4)	0.7614 (4)	123 (18)	188 (15)	195 (15)	-23 (13)	-67 (13)	-52 (13)
O4	0.5379 (5)	0.9467 (5)	0.6696 (4)	154 (18)	184 (15)	194 (16)	-41 (13)	-84 (13)	-53 (13)
O5	0.9454 (5)	0.7219 (5)	0.4514 (5)	169 (19)	253 (17)	184 (16)	-50 (15)	-73 (13)	-50 (13)
O6	0.7098 (5)	0.5161 (5)	0.2416 (5)	257 (21)	182 (16)	202 (17)	-89 (15)	-75 (15)	-16 (14)
O7	0.5984 (5)	0.8262 (5)	0.0245 (5)	193 (20)	245 (17)	213 (16)	-36 (15)	-80 (14)	-65 (14)
O8	0.8638 (5)	0.7902 (5)	0.1435 (4)	193 (19)	218 (16)	181 (15)	-76 (14)	-68 (13)	-61 (13)
O9	0.1933 (5)	0.8613 (4)	0.1246 (4)	204 (19)	182 (16)	188 (15)	-71 (14)	-115 (14)	-5 (13)
Ow	0.9157 (6)	0.8772 (6)	0.6838 (5)	214 (21)	359 (22)	317 (20)	-26 (17)	-95 (17)	-201 (17)
H1	1.039 (9)	0.845 (8)	0.684 (7)	160*					
H2	0.954*	0.828*	0.579*	160*					

Table 3. Selected interatomic distances [Å], bond angles [°] (with corresponding O—O or H—H distances in brackets), and distortion parameters Δ_{oct} [7] and σ_{oct}^2 [8] for $\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ and $\text{Ni}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ (* not refined)

	Co	Ni	angle [°], edge [Å]	Co	Ni	Co	Ni	
distance [Å]	Co	Ni		Co	Ni	Co	Ni	
Me1-O9 2x	2.028(2)	2.025(4)	09-Me1-O8 2x	86.3(1)	[2.840(3)]	06-Me2-O2 2x	84.5(1)	[2.775(3)]
Me1-O8 2x	2.125(2)	2.076(3)	09-Me1-O8 2x	93.7(1)	[3.031(3)]	06-Me2-O2 2x	95.6(1)	[3.057(4)]
Me1-O3 2x	2.199(2)	2.139(3)	09-Me1-O3 2x	89.4(1)	[2.976(4)]	06-Me2-O1 2x	87.9(1)	[2.916(3)]
<Me1-O>	2.117	2.080	09-Me1-O3 2x	90.6(1)	[3.007(3)]	06-Me2-O1 2x	92.1(1)	[3.025(4)]
Δ_{oct}	0.00109	0.00050	08-Me1-O3 2x	80.2(1)	[2.784(3)]	02-Me2-O1 2x	88.4(1)	[2.946(3)]
Me2-O6 2x	2.051(2)	2.040(3)	08-Me1-O3 2x	99.8(1)	[3.309(4)]	02-Me2-O1 2x	91.7(1)	[3.032(3)]
Me2-O2 2x	2.077(2)	2.014(3)	σ_{oct}^2	40.4		σ_{oct}^2	13.8	
Me2-O1 2x	2.149(2)	2.124(3)	Ow-Me3-O7	164.6(1)	[2.893(4)]	05-Me4-O2	99.2(1)	[3.033(3)]
<Me2-O>	2.092	2.060	Ow-Me3-O7	88.9(1)	[3.163(4)]	05-Me4-O8	89.3(1)	[2.853(4)]
Δ_{oct}	0.00039	0.00052	Ow-Me3-O1	98.5(1)	[2.961(3)]	05-Me4-O3	98.9(1)	[3.114(3)]
Me3-Ow	2.030(2)	1.995(4)	Ow-Me3-O4	89.8(1)	[2.903(6)]	05-Me4-O4	168.2(1)	
Me3-O7	2.072(2)	2.038(4)	Ow-Me3-O9	83.7(1)	[2.804(4)]	02-Me4-O8	92.0(1)	[3.169(3)]
Me3-O7	2.101(2)	2.064(4)	07-Me3-O7	79.3(1)	[2.663(5)]	02-Me4-O3	156.7(1)	
Me3-O1	2.145(2)	2.134(3)	07-Me3-O1	91.1(1)	[3.010(4)]	02-Me4-O4	88.7(1)	[2.966(3)]
Me3-O4	2.162(2)	2.154(3)	07-Me3-O4	100.2(1)	[3.248(3)]	02-Me4-O4	68.6(1)	[2.505(3)]
Me3-O9	2.171(2)	2.101(4)	07-Me3-O9	88.1(1)	[2.950(3)]	08-Me4-O3	83.3(1)	[2.784(3)]
<Me3-O>	2.114	2.081	07-Me3-O1	165.5(1)		08-Me4-O4	96.1(1)	[3.208(3)]
Δ_{oct}	0.00058	0.00070	07-Me3-O4	91.2(1)	[3.045(4)]	08-Me4-O4	178.6(1)	
Me4-O5	1.983(2)	1.987(4)	07-Me3-O9	97.3(1)	[3.208(3)]	03-Me4-O4	71.4(1)	[2.542(3)]
Me4-O2	2.002(2)	2.001(3)	01-Me3-O9	101.3(1)	[3.330(3)]	03-Me4-O4	96.0(1)	[3.364(4)]
Me4-O8	2.076(2)	2.035(3)	04-Me3-O9	71.3(1)	[2.516(3)]	04-Me4-O4	82.5(1)	[3.062(5)]
Me4-O3	2.115(2)	2.074(3)	σ_{oct}^2	78.8		σ_{oct}^2	146.6	
Me4-O4	2.403(2)	2.301(3)	02-Se1-O3	103.8(1)	[2.687(3)]	06-Se2-O8	103.6(1)	[2.647(3)]
<Me4-O>	2.136	2.091	02-Se1-O4	93.7(1)	[2.505(3)]	06-Se2-O7	104.9(1)	[2.673(4)]
Δ_{oct}	0.00463	0.00265	03-Se1-O4	95.4(1)	[2.542(3)]	08-Se2-O7	100.6(1)	[2.634(3)]
Se1-O2	1.706(2)	1.713(3)	<O-Se1-O>	97.6		<O-Se2-O>	103.0	
Se1-O3	1.709(2)	1.714(3)	05-Se3-O1	100.7(1)	[2.618(3)]			
Se1-O4	1.728(2)	1.746(3)	05-Se3-O9	104.6(1)	[2.703(4)]			
<Se1-O>	1.714	1.724	01-Se3-O9	94.6(1)	[2.516(3)]			
Se2-O6	1.658(2)	1.652(3)	<O-Se3-O>	100.0				
Se2-O8	1.711(2)	1.714(4)	distance [Å]	Co	Ni	angle [°], edge [Å]	Co	Ni
Se2-O7	1.713(2)	1.699(4)	Ow-H1	0.75(5)	0.92(7)	H1-Ow-H2	116.8(54)	[1.27(6)]
<Se2-O>	1.694	1.688	Ow-H2	0.74(4)	0.97*	Ow-H1-O3	169.1(26)	[2.802(3)]
Se3-O5	1.698(2)	1.685(4)	H1-O3	2.06(5)	1.96(7)	Ow-H2-O5	172.4(25)	[2.600(4)]
Se3-O1	1.702(2)	1.704(4)	H2-O5	1.86(4)	1.64*			
Se3-O9	1.720(2)	1.721(3)						
<Se3-O>	1.707	1.703						

Preliminary X-ray investigations were done using rotation and Weissenberg photographs. Unit cell dimensions [refined from 34, 43 accurate 2θ values in the range $24^\circ < 2\theta < 48^\circ$] and X-ray intensities were measured on a four-circle diffractometer; for detailed information see Table 1. Corrections were applied for absorption, and for Lorentz and polarization effects. For $\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ the Co and Se atoms were located by direct methods, the positions of O and H atoms were revealed by Fourier and difference Fourier summations. Complex neutral atomic scattering curves [4] were used. The least-squares refinement, including anisotropic thermal parameters (isotropic for H atoms) and an extinction correction [5], converged to $R_w = 0.023$. For the refinement of $\text{Ni}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ the atomic coordinates of $\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ were used as starting positions. In the Ni compound the hydrogen atom H2 could not be refined, but was located in the difference Fourier map and fixed at this position. The thermal parameters of both hydrogens were also fixed in the refinement. The final R_w -factor is 0.032. The atomic coordinates and thermal parameters for both compounds are listed in Table 2.

Results and Discussion

General Description

Table 3 gives information on important bond lengths [\AA] and angles [$^\circ$], and lists the distortion parameters Δ_{oct} [7] and σ_{oct}^2 [8]. The *Me1* and *Me2* atoms are situated at centers of inversion, all other atoms occupy a position with site symmetry 1.

The structure consists of $[\text{Me}(1/3/4)_3(\text{Se}(1/2/3)\text{O}_3)_6 \cdot 2\text{H}_2\text{O}]^{2-}$ sheets parallel (010); one such sheet is shown in Fig. 1. Paying special attention to the

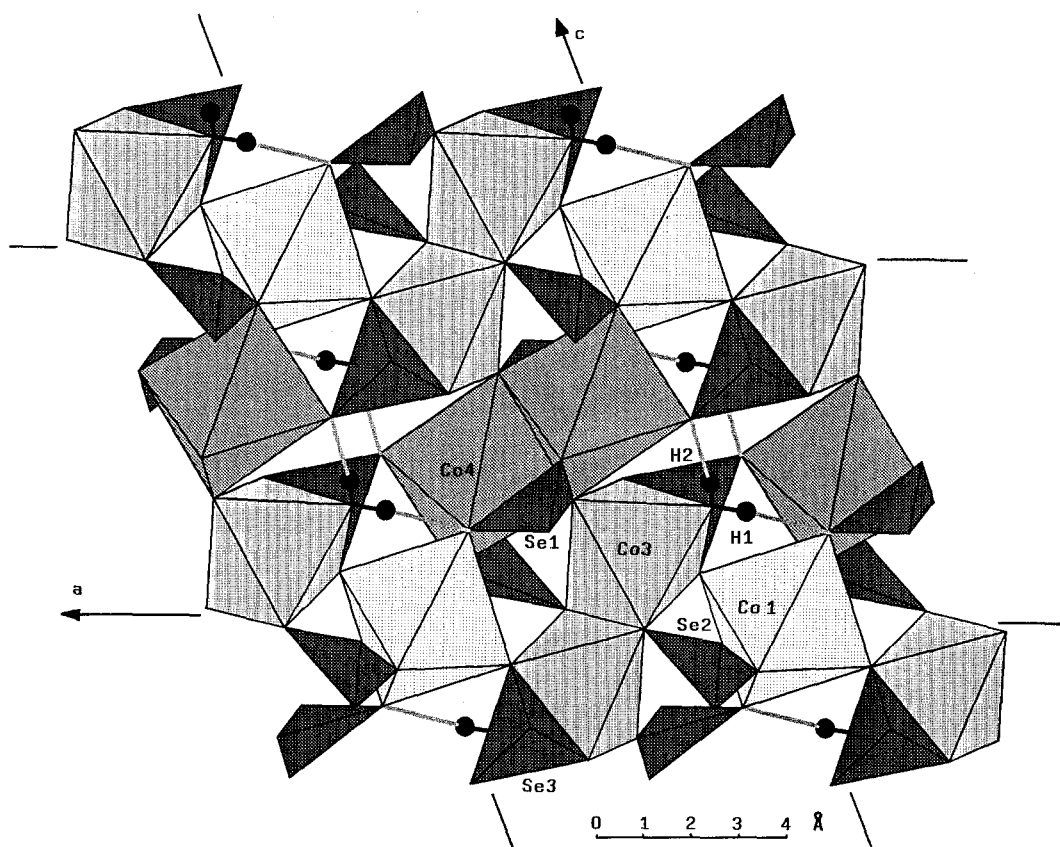


Fig. 1. Projection of the crystal structure of $\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ along $[010]$, showing a single sheet

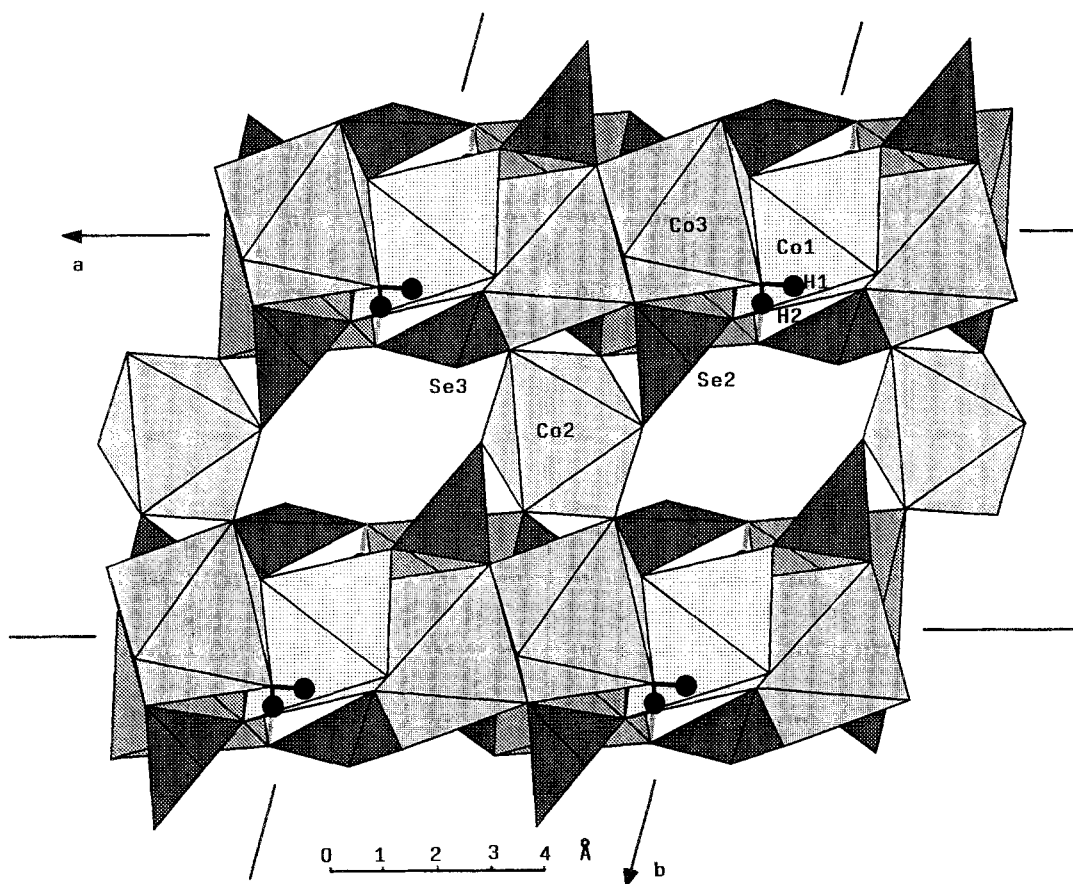


Fig. 2. Projection of the crystal structure of $\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ along $[001]$

edge connections of the coordination polyhedra, these sheets can be described to be composed of closely packed $[\text{Me}(1/4)_3(\text{Se}(1)\text{O}_3)_2]^{2+}$ chains and $[\text{Me}(3)_2(\text{Se}(3)\text{O}_3)_2 \cdot 2\text{H}_2\text{O}]^0$ groups. The chains are corner-connected to the groups, further linkage results from hydrogen bonds and from $\text{Se}(2)\text{O}_3$ groups, which share each one corner with a chain and with a group within the sheet, whereas the third corner belongs to a $\text{Me}(2)\text{O}_6$ octahedron. These octahedra are the only connection between consecutive sheets. The remaining free space between the sheets is occupied by the lone-pair electrons of the Se^{4+} atoms (see Fig. 2).

The Coordination Polyhedra

All Me^{2+} atoms have a distorted octahedral environment. The $\text{Me}1$ atoms are $[2+2+2]$ coordinated, with a smaller bond length distortion in the Ni compound; the bond angle distortions are moderate, and similar in both compounds. All corners are shared with SeO_3 groups, two corners are also in common with $\text{Me}(3)\text{O}_6$ octahedra; the two edges shared with $\text{Me}(4)\text{O}_6$ octahedra and the corresponding angles are the smallest within the $\text{Me}(1)\text{O}_6$ octahedra, whereas the edges running approximately parallel to the direction of the chain are the longest ones. The O3 atom further acts as acceptor (of H1) in a hydrogen bond.

The *Me2* atoms are [4 + 2] coordinated, forming octahedra with moderate bond length and small bond angle distortions [it is worth mentioning that the elongation of the Ni(2)O₆ octahedron is more pronounced compared to the corresponding CoO₆ octahedron]. These octahedra connect consecutive sheets by sharing their corners with six SeO₃ pyramids, four corners are in addition shared with two *Me(3)O₆* and two *Me(4)O₆* polyhedra, respectively.

Contrary to crystal chemical expectations, the bond length distortion within the *Me(3)O₆* polyhedra is again, as for the *Me2* environments, stronger for the Ni(3)O₆ than for the Co(3)O₆ polyhedra. The bond angle distortion, which is slightly smaller in the Ni compound, is mainly caused by polyhedral interconnections: The shortest edge (O1 – O9) is shared with a Se(3)O₃ pyramid and the corresponding angles are $\approx 72^\circ$. A second edge (O7 – O7) is shared with another *Me(3)O₆* octahedron, building up the groups mentioned above. The *Me(3)O₆* octahedron further shares corners with a *Me(1)O₆* octahedron (O9), a *Me(2)O₆* octahedron (O1), two Se(2)O₃ groups (2 × O7), and O4 is in common with two *Me(4)O₆* octahedra and a Se(1)O₃ pyramid. Ow is donor for the hydrogen bonds of the water molecule.

The extreme bond length and bond angle distortions of the *Me(4)O₆* and Se(1)O₃ polyhedra are correlated with their uncommon polyhedral connection: each *Me(4)O₆* octahedron shares an edge (O4 – O4) with a second *Me(4)O₆* octahedron and two Se(1)O₃ pyramids are wedged in the notches between them, each pyramid sharing two of its edges (O2 – O4, O3 – O4) with a *Me(4)₂O₁₀* pair. These edges are by far the shortest within the octahedron, the bond angles are reduced to values from 68.6(1)° to 74.0(2)°. The corresponding O – Se – O angles are also reduced from average 101° (as given by Fischer and Zemann [9]) to values as small as 92.8(2)°, whereas the third angle of the Se(1)O₃ pyramid is extended to about 104° [O – Se⁴⁺ – O bond angles smaller than 95° are rare in crystal structures; another example is found in Li₂Cu₃(SeO₃)(SeO₄)₂ [10], where the smallest O – Se⁴⁺ – O angle is 90.7(1)°]. The bond angle distortion parameters σ_{oct}^2 for the *Me(4)O₆* polyhedra are 146.6 and 117.8, respectively. CoO₆ and especially NiO₆ octahedra with a bond angle distortion of this magnitude are rarely reported in literature [e.g. 11 – 19]. *Me4*–O distances range from 1.983 (2), 1.987 (4) Å (*Me4*–O5) to 2.403 (2), 2.301 (3) Å (*Me4*–O4), the distortion parameters Δ_{oct} are 0.00463 and 0.00265, respectively. To the authors best knowledge there exist only two cases of CoO₆ octahedra among well refined crystal structures with a higher Δ_{oct} parameter, namely in Co₅(PO₄)₂(OH)₄ [17] ($\Delta_{\text{oct}} = 0.00474$, Co – O distances from 1.983 Å to 2.410 Å) and in Co₂Si₂O₆ [18] ($\Delta_{\text{oct}} = 0.00832$, distances from 1.982 Å to 2.517 Å). Apart from the mentioned polyhedral connections, each *Me(4)O₆* octahedron is further linked with a Co(1)O₆ octahedron (by a common edge O3 – O8) and with a Se(2)O₃ group, a Se(3)O₃ group, one *Me(2)O₆* and two *Me(3)O₆* octahedra (by common corners). O3 and O5 are in addition acceptors of hydrogen bonds.

Contrary to the Se(1)O₃ groups, which have mean bond angles of about 97°, the Se(2)O₃ pyramids are stretched between the structural units and therefore somewhat flattened: in both compounds the mean bond angle is 103.0°; the Se(3)O₃ groups share their shortest edge with the *Me(3)O₆* octahedra.

The hydrogen bonding system in *Me₃(SeO₃)₃ · H₂O* increases the stability within the [*Me₃(SeO₃)₆ · 2H₂O*]²⁻ sheets; there exist no hydrogen bonds between consecutive sheets. A feature worth mentioning is a very short hydrogen bond (Ow – O5): it is 2.600(4) Å in the Co compound and even only 2.561(6) Å in the

Table 4. Bond valences ν [v. u.] [6] calculated (without H atoms) for the oxygen atoms in $\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ and $\text{Ni}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$

$\Sigma\nu$	O1	O2	O3	O4	O5	O6	O7	O8	O9	Ow
Co	1.83	2.02	1.80	1.84	1.71	1.76	1.90	1.88	1.87	0.40
Ni	1.79	1.97	1.80	1.83	1.70	1.75	1.93	1.88	1.85	0.40

Ni compound. The latter is one of the shortest known hydrogen bonds donated by a water molecule. Chiari and Ferraris [20] found 2.546 Å as lower limit for such bonds, in the very most cases these bonds are > 2.60 Å. Supposing 3.148 Å as reasonable upper limit, Chiari and Ferraris found 2.805 Å as average value for 298 hydrogen bonds of H_2O molecules, and the second hydrogen bond length (Ow – O3) is near to this value in both compounds. The functions of Ow, O3 and O5 in the hydrogen bonding scheme can be correlated with bond valence calculations [6] for the oxygen atoms (see Table 4). A possible involvement of O1, O4 and O6 in the hydrogen bonding scheme, which might be derived from these calculations, can be excluded from geometrical and crystal chemical considerations.

Most of the oxygen atoms in the title compounds are threefold coordinated (namely O1, O2, O5, O7, O8, O9, Ow) forming slightly pyramidal to nearly planar arrangements. O3 and O4 are coordinated by four cations in a strongly distorted tetrahedral configuration. O6 is only coordinated by one Me2 and one Se2 atom with a bond angle of $\approx 141^\circ$.

The ellipsoids of the thermal motion comply with common experience. For the Co, Ni and Se atoms they are nearly spherically shaped, the oxygens of the water molecules have the strongest anisotropy in both compounds, the ratio of the longest to shortest ellipsoid axis being approximately 1.6.

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