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Crystal Structures of $Co_3(SeO_3)_3 \cdot H_2O$ and $Ni_3(SeO_3)_3 \cdot H_2O$, Two New Isotypic Compounds

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Summary. The crystal structures of the new, hydrothermally synthesized, isotypic compounds $Co_3(SeO_3)_3 \cdot H_2O$ and $Ni_3(SeO_3)_3 \cdot H_2O$ were determined by direct and Fourier methods and refined to $R_w = 0.023$, 0.032 using single crystal X-ray data up to $\sin\theta/\lambda = 0.81$ Å^{-1} [space group $P\bar{1}$, $a = 8.102$ (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 $[Me_5(SeO_3)_6 \cdot 2H_2O]^{2-}$ 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 $Me^{2+[6]}$ atom. All coordination polyhedra deviate significantly from their ideal shapes, bond lengths within the extremly distorted $Me(4)O_6$ polyhedra range from 1.983 (2) Å to 2.403 (2) Å in $Co_3(SeO_3)_3 \cdot H_2O$ 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 $Ni_3(SeO_3)_3 \cdot H_2O$. The latter is one of the shortest known hydrogen bonds donated by a water molecule.

Keywords. $Co_3(SeO_3)_3 \cdot H_2O$; $Ni_3(SeO_3)_3 \cdot H_2O$; Crystal structure; Crystal chemistry; Short hydrogen bonds.

Die Kristallstrukturen von $Co_3(SeO_3)_3 \cdot H_2O$ und $Ni_3(SeO_3)_3 \cdot H_2O$, zwei neue isotype Verbindungen

Zusammenfassung. Die Kristallstrukturen der neuen, hydrothermal synthetisierten, isotypen Verbindungen $Co_3(SeO_3)_3 \cdot H_2O$ und $Ni_3(SeO_3)_3 \cdot H_2O$ wurden mit direkten und Fourier-Methoden bestimmt und unter Verwendung von Einkristallröntgendaten bis $\sin\theta/\lambda = 0.81$ Å^{-1} auf R_w-Werte von 0.023, 0.032 verfeinert [Raumgruppe $P\bar{1}$, $a = 8.102$ (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 $[Me_5(SeO_3)_6 \cdot 2H_2O]^{2-}$ 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 $Me^{2+[6]}$ Atomen verknüpft. Alle Koordinationspolyeder weichen deutlich von ihren Idealformen ab, Bindungslängen in den extrem verzerrten $Me(4)O_6$ Polyedern variieren zwischen 1.983 (2) Å und 2.403 (2) Å in $Co_3(SeO_3)_3 \cdot H_2O$ 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 $Ni_3(SeO_3)_3 \cdot H_2O$. 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 $NaCo_2(SeO_3)_2(OH)$ [1, 2] and of $CoSeO_3 \cdot 2H_2O$ and $NiSeO_3 \cdot 2H_2O$

[3] were determined or refined previously. Recently, single crystals of $Co_3(SeO_3)_3 \cdot H_2O$ 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 isotypic compound containing a Me^{2+} ion that (1) prefers a more regular octahedral coordination and (2) is smaller than the Co^{2+} ion. Therefore attemps were made to obtain the isotypic Ni compound, $Ni_3(SeO_3)_3 \cdot H_2O$.

Experimental

Crystals of the title compounds were synthesized under hydrothermal conditions. Teflon lined steel vessels ($V \approx 4\,cm^3$) were filled with ≈ 0.5 g of approximately equimolar amounts of $Co(OH)_2$, $KHCO_3$ 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 ≈ 210°C and kept at this temperature for five days. Dark violet, pleochroic crystals of $Co_3(SeO_3)_3 \cdot H_2O$ up to ≈ 0.3 mm and yellow crystals of $Ni_3(SeO_3)_3 \cdot H_2O$ up to ≈ 0.2 mm were obtained. Predominant forms of the platelike crystals are {001} (Co) and {011} (Ni).

Table 1. Cell parameters of $Co_3(SeO_3)_3 \cdot H_2O$ and $Ni_3(SeO_3)_3 \cdot H_2O$ and details of X-ray data collections and structure refinements

Compound	$Co_3(SeO_3)_3 \cdot H_2O$	$Ni_3(SeO_3)_3 \cdot H_2O$
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	8.102 (2)	7.986 (3)
b [Å]	8.219 (2)	8.133 (3)
c [Å]	8.572 (2)	8.422 (3)
α [°]	69.15 (1)	69.50 (1)
β [°]	62.88 (1)	62.50 (1)
γ [°]	67.23 (1)	67.64 (1)
V [$Å^3$]	457.10	438.41
Formula units per cell	2	2
Calculated density ρ_{calc} [$g\,cm^{-3}$]	4.18	4.36
Absorption coefficient $\mu(MoK\alpha)$ [cm^{-1}]	168.86	183.60
Equipment	Stoe four circle diffractometer AED2; graphite monochromatized MoKα-radiation; program system STRUCSY (Stoe & Cie, Darmstadt, FRG)	
Data collection	2θ-ω scans; 45, 48 steps/reflection, increased for $\alpha_1 - \alpha_2$ splitting; 0.03° and 0.5 – 1.5 s/step; 2*7, 8 steps for background measurements; 3, 4 standard reflections each 120 min; $2\theta_{max} = 70.0°$	
Crystal dimensions [mm]	0.18 × 0.10 × 0.04	0.15 × 0.10 × 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 $Co_3(SeO_3)_3 \cdot H_2O$ and $Ni_3(SeO_3)_3 \cdot H_2O$ with e.s.d.'s in parentheses. Given U_{ij} are multiplied by 10^4 (* fixed in the final refinement). $ATF = \exp[-2\pi^2 \Sigma_{i=1}^{3} \Sigma_{j=1}^{3} U_{ij} a_i^* a_j^* h_i h_j]$

Atom	x/a	y/b	z/c	U_{11}/U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$Co_3(SeO_3)_3 \cdot H_2O$									
Co1	0	0	0	116 (2)	146 (2)	134 (3)	−42 (2)	−44 (2)	−15 (2)
Co2	½	½	½	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	½	½	½	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^2_{oct} [8] for $Co_3(SeO_3)_3 \cdot H_2O$ and $Ni_3(SeO_3)_3 \cdot H_2O$ (* not refined)

distance[Å]	Co	Ni
Me1-O9 2x	2.028(2)	2.025(4)
Me1-O8 2x	2.125(2)	2.076(3)
Me1-O3 2x	2.199(2)	2.139(3)
<Me1-O>	2.117	2.080
Δ_{oct}	0.00109	0.00050
Me2-O6 2x	2.051(2)	2.040(3)
Me2-O2 2x	2.077(2)	2.014(3)
Me2-O1 2x	2.149(2)	2.124(3)
<Me2-O>	2.092	2.060
Δ_{oct}	0.00039	0.00052
Me3-Ow	2.030(2)	1.995(4)
Me3-O7	2.072(2)	2.038(4)
Me3-O7	2.101(2)	2.064(4)
Me3-O1	2.145(2)	2.134(3)
Me3-O4	2.162(2)	2.154(3)
Me3-O9	2.171(2)	2.101(4)
<Me3-O>	2.114	2.081
Δ_{oct}	0.00058	0.00070
Me4-O5	1.983(2)	1.987(4)
Me4-O2	2.002(2)	2.001(3)
Me4-O8	2.076(2)	2.035(3)
Me4-O3	2.115(2)	2.074(3)
Me4-O4	2.403(2)	2.301(3)
<Me4-O>	2.136	2.091
Δ_{oct}	0.00463	0.00265
Se1-O2	1.706(2)	1.713(3)
Se1-O3	1.709(2)	1.714(3)
Se1-O4	1.728(2)	1.746(3)
<Se1-O>	1.714	1.724
Se2-O6	1.658(2)	1.652(3)
Se2-O8	1.711(2)	1.714(4)
Se2-O7	1.713(2)	1.699(4)
<Se2-O>	1.694	1.688
Se3-O5	1.698(2)	1.685(4)
Se3-O1	1.702(2)	1.704(4)
Se3-O9	1.720(2)	1.721(3)
<Se3-O>	1.707	1.703

angle[°],edge[Å]	Co	Ni		Co	Ni
O9-Me1-O8 2x	86.3(1) [2.840(3)]	87.2(2) [2.827(6)]	O6-Me2-O2 2x	84.5(1) [2.775(3)]	84.4(2) [2.721(6)]
O9-Me1-O8 2x	93.7(1) [3.031(3)]	92.8(2) [2.971(5)]	O6-Me2-O2 2x	95.6(1) [3.057(4)]	95.7(2) [3.004(5)]
O9-Me1-O3 2x	89.4(1) [2.976(4)]	89.2(2) [2.924(5)]	O6-Me2-O1 2x	87.9(1) [2.916(3)]	88.1(2) [2.896(6)]
O9-Me1-O3 2x	90.6(1) [3.007(3)]	90.8(2) [2.965(5)]	O6-Me2-O1 2x	92.1(1) [3.025(4)]	91.9(2) [2.992(5)]
O8-Me1-O3 2x	80.2(1) [2.784(3)]	80.6(2) [2.727(5)]	O2-Me2-O1 2x	88.4(1) [2.946(3)]	88.2(2) [2.880(6)]
O8-Me1-O3 2x	99.8(1) [3.309(4)]	99.4(2) [3.214(5)]	O2-Me2-O1 2x	91.7(1) [3.032(3)]	91.8(2) [2.973(5)]
σ_{oct}^2	40.4	35.2	σ_{oct}^2	13.8	14.1
Ow-Me3-O7	164.6(1)	165.8(2)	O5-Me4-O2	99.2(1) [3.033(3)]	94.8(2) [2.936(6)]
Ow-Me3-O7	88.9(1) [2.893(4)]	88.9(2) [2.842(6)]	O5-Me4-O8	89.3(1) [2.853(4)]	87.4(2) [2.780(6)]
Ow-Me3-O1	98.5(1) [3.163(4)]	97.8(2) [3.113(6)]	O5-Me4-O3	98.9(1) [3.114(3)]	99.8(2) [3.106(5)]
Ow-Me3-O4	89.8(1) [2.961(3)]	88.7(2) [2.903(6)]	O5-Me4-O4	168.2(1)	171.7(2)
Ow-Me3-O9	83.7(1) [2.804(4)]	84.5(2) [2.754(6)]	O5-Me4-O4	92.0(1) [3.169(3)]	92.3(2) [3.101(6)]
O7-Me3-O7	79.3(1) [2.663(5)]	80.6(2) [2.653(8)]	O2-Me4-O8	111.6(1) [3.374(4)]	108.5(2) [3.275(5)]
O7-Me3-O1	91.1(1) [3.010(4)]	90.9(2) [2.975(6)]	O2-Me4-O3	156.7(1)	161.8(2)
O7-Me3-O4	100.2(1) [3.248(3)]	100.9(2) [3.232(5)]	O2-Me4-O4	88.7(1) [2.966(3)]	90.4(2) [2.944(5)]
O7-Me3-O9	88.1(1) [2.950(3)]	87.6(2) [2.864(6)]	O2-Me4-O4	68.6(1) [2.505(3)]	70.8(2) [2.505(5)]
O7-Me3-O1	165.5(1)	167.5(2)	O8-Me4-O3	83.3(1) [2.784(3)]	83.1(2) [2.727(5)]
O7-Me3-O4	91.2(1) [3.045(4)]	91.0(2) [3.008(6)]	O8-Me4-O4	96.1(1) [3.208(3)]	97.1(2) [3.134(5)]
O7-Me3-O9	97.3(1) [3.208(3)]	97.8(2) [3.139(6)]	O8-Me4-O4	178.6(1)	179.2(2)
O1-Me3-O4	101.3(1) [3.330(3)]	99.7(2) [3.276(6)]	O3-Me4-O4	71.4(1) [2.542(3)]	74.0(2) [2.540(6)]
O1-Me3-O9	71.3(1) [2.516(3)]	72.5(2) [2.505(6)]	O3-Me4-O4	96.0(1) [3.364(4)]	97.6(1) [3.296(5)]
O4-Me3-O9	169.2(1)	168.8(2)	O4-Me4-O4	82.5(1) [3.062(5)]	83.3(2) [2.967(8)]
σ_{oct}^2	78.8	69.9	σ_{oct}^2	146.6	117.8
O2-Se1-O3	103.8(1) [2.687(3)]	104.3(2) [2.705(5)]	O6-Se2-O8	103.6(1) [2.647(3)]	103.9(2) [2.650(6)]
O2-Se1-O4	93.7(1) [2.505(3)]	92.8(2) [2.505(5)]	O6-Se2-O7	104.9(1) [2.673(4)]	104.9(2) [2.657(6)]
O3-Se1-O4	95.4(1) [2.542(3)]	94.4(2) [2.540(6)]	O8-Se2-O7	100.6(1) [2.634(3)]	100.3(2) [2.621(6)]
<O-Se1-O>	97.6	97.2	<O-Se2-O>	103.0	103.0
O5-Se3-O1	100.7(1) [2.618(3)]	101.3(2) [2.621(6)]			
O5-Se3-O9	104.6(1) [2.703(4)]	104.7(2) [2.696(6)]			
O1-Se3-O9	94.6(1) [2.516(3)]	94.0(2) [2.505(6)]			
<O-Se3-O>	100.0	100.0			

distance[Å]	Co	Ni
Ow-H1	0.75(5)	0.92(7)
Ow-H2	0.74(4)	0.97*
H1-O3	2.06(5)	1.96(7)
H2-O5	1.86(4)	1.64*

angle[°],edge[Å]	Co	Ni
H1-Ow-H2	116.8(54) [1.27(6)]	96.1* [1.40*]
Ow-H1-O3	169.1(26) [2.802(3)]	145.5(49) [2.762(6)]
Ow-H2-O5	172.4(25) [2.600(4)]	158.9* [2.561(6)]

Preliminary X-ray investigations were done using rotation and Weissenberg photographs. Unit cell dimensions [refined from 34, 43 accurate 2θ values in the range $24° < 2\theta < 48°$] and X-ray intensities were measured on a four-circle diffractometer; for detailed information see Table1. Corrections were applied for absorption, and for Lorentz and polarization effects. For $Co_3(SeO_3)_3 \cdot H_2O$ 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 $Ni_3(SeO_3)_3 \cdot H_2O$ the atomic coordinates of $Co_3(SeO_3)_3 \cdot H_2O$ 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 Table2.

Results and Discussion

General Description

Table3 gives information on important bond lengths [Å] and angles [°], and lists the distortion parameters Δ_{oct} [7] and σ^2_{oct} [8]. The *Me*1 and *Me*2 atoms are situated at centers of inversion, all other atoms occupy a position with site symmetry 1.

The structure consists of $[Me(1/3/4)_5(Se(1/2/3)O_3)_6 \cdot 2H_2O]^{2-}$ sheets parallel (010); one such sheet is shown in Fig. 1. Paying special attention to the

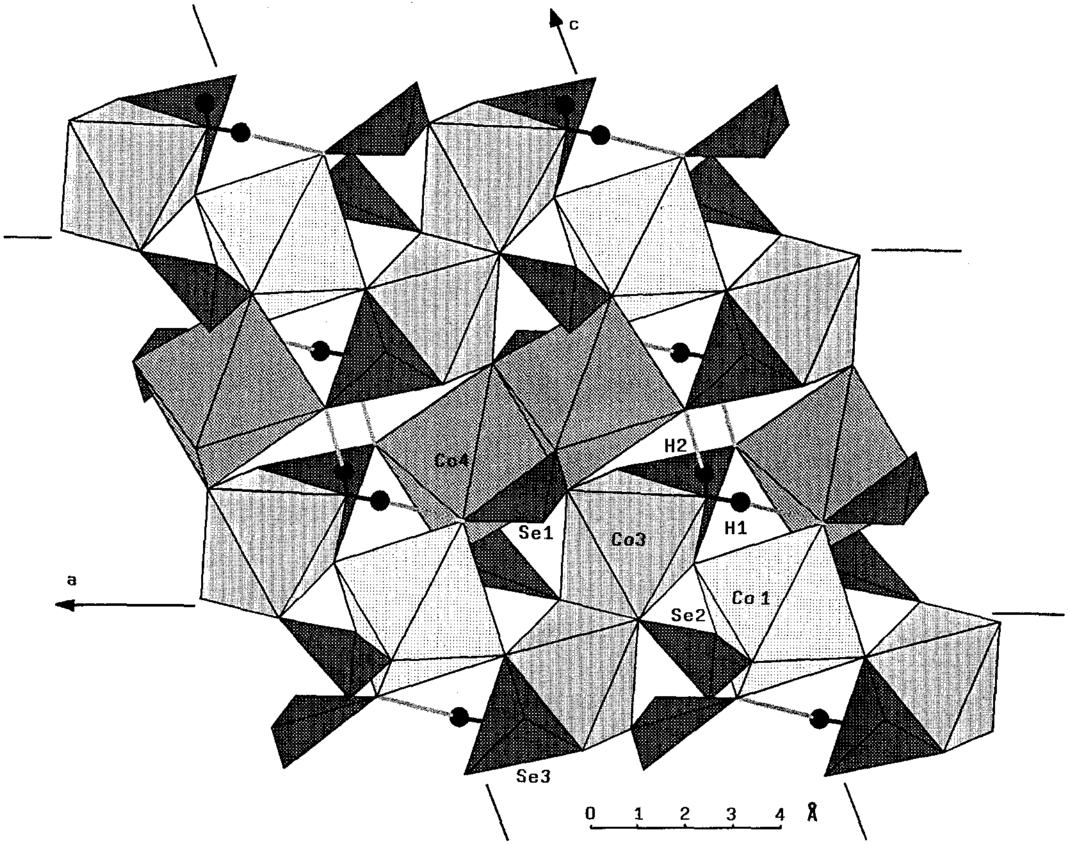

Fig. 1. Projection of the crystal structure of $Co_3(SeO_3)_3 \cdot H_2O$ along [010], showing a single sheet

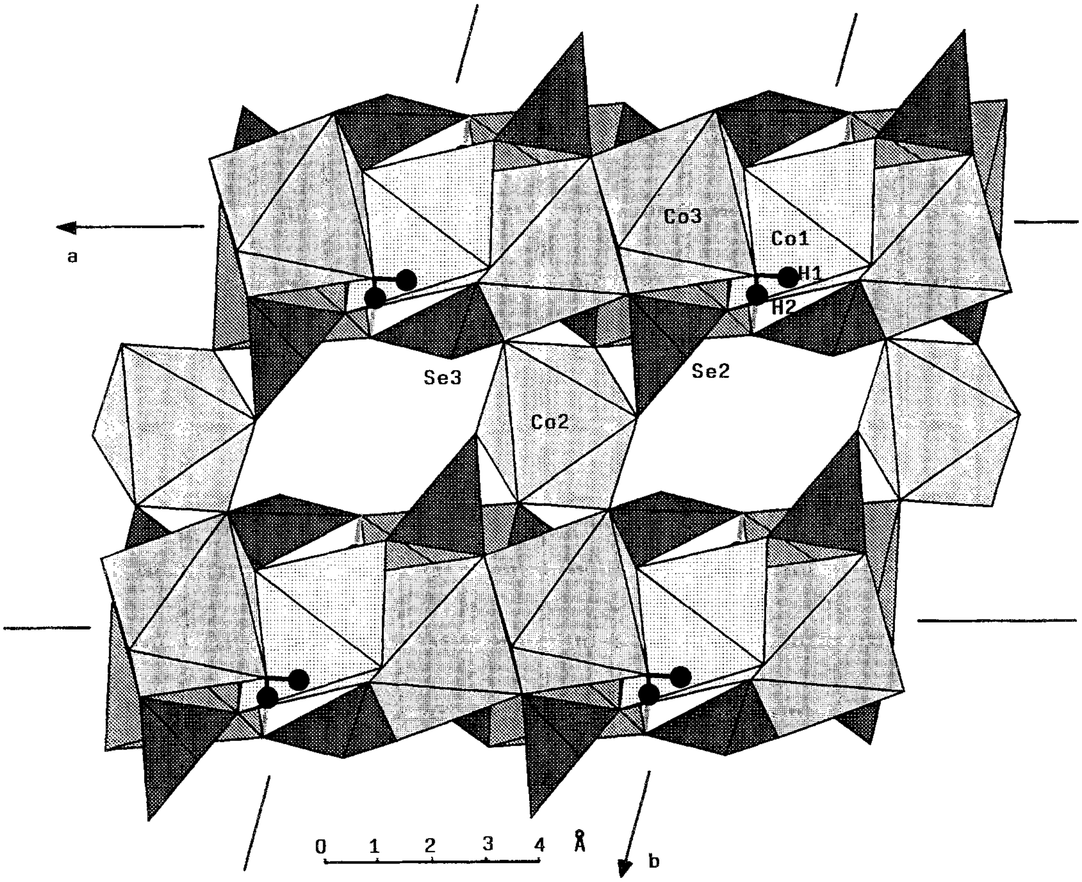

Fig. 2. Projection of the crystal structure of $Co_3(SeO_3)_3 \cdot H_2O$ along [001]

edge connections of the coordination polyhedra, these sheets can be described to be composed of closely packed $[Me(1/4)_3(Se(1)O_3)_2]^{2+}$ chains and $[Me(3)_2(Se(3)O_3)_2 \cdot 2\,H_2O]^0$ groups. The chains are corner-connected to the groups, further linkage results from hydrogen bonds and from $Se(2)O_3$ groups, which share each one corner with a chain and with a group within the sheet, whereas the third corner belongs to a $Me(2)O_6$ 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 *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 $Me(3)O_6$ octahedra; the two edges shared with $Me(4)O_6$ octahedra and the corresponding angles are the smallest within the $Me(1)O_6$ 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 *Me*2 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)O_6 octahedron is more pronounced compared to the corresponding CoO_6 octahedron]. These octahedra connect consecutive sheets by sharing their corners with six SeO_3 pyramids, four corners are in addition shared with two *Me*(3)O_6 and two *Me*(4)O_6 polyhedra, respectively.

Contrary to crystal chemical expectations, the bond length distortion within the *Me*(3)O_6 polyhedra is again, as for the *Me*2 environments, stronger for the Ni(3)O_6 than for the Co(3)O_6 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)O_3 pyramid and the corresponding angles are ≈72°. A second edge (O7 − O7) is shared with another *Me*(3)O_6 octahedron, building up the groups mentioned above. The *Me*(3)O_6 octahedron further shares corners with a *Me*(1)O_6 octahedron (O9), a *Me*(2)O_6 octahedron (O1), two Se(2)O_3 groups (2 × O7), and O4 is in common with two *Me*(4)O_6 octahedra and a Se(1)O_3 pyramid. Ow is donator for the hydrogen bonds of the water molecule.

The extreme bond length and bond angle distortions of the *Me*(4)O_6 and Se(1)O_3 polyhedra are correlated with their uncommon polyhedral connection: each *Me*(4)O_6 octahedron shares an edge (O4 − O4) with a second *Me*(4)O_6 octahedron and two Se(1)O_3 pyramids are wedged in the notches between them, each pyramid sharing two of its edges (O2 − O4, O3 − O4) with a *Me*(4)$_2O_{10}$ 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)O_3 pyramid is extended to about 104° [$O-Se^{4+}-O$ bond angles smaller than 95° are rare in crystal structures; another example is found in $Li_2Cu_3(SeO_3)(SeO_4)_2$ [10], where the smallest $O-Se^{4+}-O$ angle is 90.7(1)°]. The bond angle distortion parameters σ^2_{oct} for the *Me*(4)O_6 polyhedra are 146.6 and 117.8, respectively. CoO_6 and especially NiO_6 octahedra with a bond angle distortion of this magnitude are rarely reported in literature [e.g. 11 − 19]. *Me*4-O distances range from 1.983(2), 1.987(4) Å (*Me*4-O5) to 2.403(2), 2.301(3) Å (*Me*4-O4), the distortion parameters Δ_{oct} are 0.00463 and 0.00265, respectively. To the authors best knowledge there exist only two cases of CoO_6 octahedra amoung well refined crystal structures with a higher Δ_{oct} parameter, namely in $Co_5(PO_4)_2(OH)_4$ [17] ($\Delta_{oct}=0.00474$, Co − O distances from 1.983 Å to 2.410 Å) and in $Co_2Si_2O_6$ [18] ($\Delta_{oct}=0.00832$, distances from 1.982 Å to 2.517 Å). Apart from the mentioned polyhedral connections, each *Me*(4)O_6 octahedron is further linked with a Co(1)O_6 octahedron (by a common edge O3 − O8) and with a Se(2)O_3 group, a Se(3)O_3 group, one *Me*(2)O_6 and two *Me*(3)O_6 octahedra (by common corners). O3 and O5 are in addition acceptors of hydrogen bonds.

Contrary to the Se(1)O_3 groups, which have mean bond angles of about 97°, the Se(2)O_3 pyramids are stretched between the structural units and therefore somewhat flattened: in both compounds the mean bond angle is 103.0°; the Se(3)O_3 groups share their shortest edge with the *Me*(3)O_6 octahedra.

The hydrogen bonding system in $Me_3(SeO_3)_3\cdot H_2O$ increases the stability within the $[Me_5(SeO_3)_6\cdot 2H_2O]^{2-}$ 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 υ [v. u.] [6] calculated (without H atoms) for the oxygen atoms in $Co_3(SeO_3)_3 \cdot H_2O$ and $Ni_3(SeO_3)_3 \cdot H_2O$

Συ	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 *Me*2 and one Se2 atom with a bond angle of ≈141°.

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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References

[1] Wildner M. (1988) Diploma Thesis. Univ. Wien
[2] Wildner M. (1988) Z. Krist. **185**: 499
[3] Wildner M. (1990) N. Jb. Miner. Mh. **1990**: 353
[4] Ibers J. A., Hamilton W. C. (eds.) (1974) International Tables for X-Ray Crystallography, Vol. IV. Kynoch Press, Birmingham
[5] Zachariasen W. H. (1967) Acta Cryst. **23**: 558
[6] Brown I. D. (1981) Structure and Bonding in Crystals, Vol. II-14. Academic Press, New York
[7] Brown I. D., Shannon R. D. (1973) Acta Cryst. **A 29**: 266
[8] Robinson K., Gibbs G. V., Ribbe P. H. (1971) Science **172**: 567
[9] Fischer R., Zemann J. (1974) Handbook of Geochemistry II-3, 34-A. Springer, Berlin Heidelberg New York

[10] Giester G. (1989) Monatsh. Chem. **120**: 661
[11] Effenberger H., Pertlik F. (1984) Z. Krist. **166**: 129
[12] Effenberger H. (in preparation) Monatsh. Chem.
[13] Krishnamachari N., Calvo C. (1972) Acta Cryst. **B28**: 2883
[14] Tordjman I., Guitel J. C., Durif A., Averbuch M. T., Masse R. (1978) Mat. Res. Bul. **13**: 983
[15] Keller P., Riffel H., Zettler F., Hess H. (1981) Z. Anorg. Allg. Chem. **474**: 123
[16] Jasper-Tönnies B., Müller-Buschbaum H. (1984) Z. Anorg. Allg. Chem. **517**: 161
[17] Ruszala F. A., Anderson J. B., Kostiner E. (1977) Inorg. Chem. **16**: 2417
[18] Sasaki S., Takéuchi Y. (1982) Z. Krist. **158**: 279
[19] Buckley A. M., Bramwell S. T., Day P. (1990) J. Sol. State Chem. **86**: 1
[20] Chiari G., Ferraris G. (1982) Acta Cryst. **B38**: 2331
[21] Wildner M. (1990) Thesis. Univ. Wien
[22] Dowty E. (1989) Atoms. A Computer Program for Displaying Atomic Structures. Shape Software, Kingsport

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