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The Synthesis and Crystal Structure of a New Nickel Selenite Hydrate, $Ni_3(SeO_3)_3 \cdot H_2O$

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The new nickel selenite hydrate of composition $Ni_3(SeO_3)_3 \cdot H_2O$ crystallizes in the triclinic space group $P\bar{1}$ with lattice constants of $a = 8.118(2)$, $b = 8.423(2)$, $c = 8.531(2)$ Å, $\alpha = 123.81(2)$, $\beta = 90.59(2)$ and $\gamma = 111.43(2)°$, $V = 438.6$ Å^3, $Z = 2$. The crystal structure of a hydrothermally grown crystal was determined and refined ($R = 2.85\%$, $R_w = 3.27\%$, $F(000) = 536$, $\rho_{calc} = 4.36$ g/cm^3, $\mu = 187$ cm^{-1}, 1968 observed reflections with $I > 3\sigma(I)$) from single crystal X-ray data. The title compound has a complex framework of edge and corner-sharing NiO_6 octahedra, crosslinked by pyrimidal SeO_3 groups. © 1991 Academic Press, Inc.

Introduction

The nickel–selenium–oxygen system has been the subject of several previous investigations and a number of phases have been reported in which Se is found in oxidation states IV or VI. Selenium (VI)-containing nickel selenate, $NiSeO_4$, which adopts the orthorhombic chromic vanadate structure, was first reported by Snyman and Pistorius (*1*). Hydrated modifications of $NiSeO_4$ have also been prepared and characterized to varying extents by the same workers (*1, 2*), including $NiSeO_4 \cdot H_2O$, which is isostructural with $NiSO_4 \cdot H_2O$, and $NiSeO_4 \cdot 6H_2O$, which was also the subject of a single-crystal investigation by Fuess (*3*). The hydrated selenates $NiSeO_4 \cdot 2H_2O$ and $NiSeO_4 \cdot 4H_2O$ were characterized on the basis on X-ray powder diffraction data and thermal analysis measurements (*1*).

The selenium(IV)-containing distorted-perovskite-type phase $NiSeO_3$ has been prepared at high temperature and pressure, and orders antiferromagnetically at 98 K (*4*). Other nickel selenites include the naturally occurring Ahlfeldite, $NiSeO_3 \cdot 2H_2O$ (*5*), which is isomorphous with other hydrated divalent selenites $MSeO_3 \cdot 2H_2O$ (M = Mg, Mn, Co, Cu, Zn), and the diselenite $NiSe_2O_5 \cdot 3H_2O$ (*6*), which adopts the same structure as its cobalt and zinc analogues. Makatan *et al.* (*7*) examined the decomposition of $NiSeO_3 \cdot 2H_2O$ as a function of temperature and found amorphous phases of approximate composition $NiSeO_3 \cdot H_2O$ and $NiSeO_3 \cdot 1/2H_2O$. Ebert *et al.* (*8*) have recently carried out infrared and thermal measurements on various nickel–selenium–oxygen phases and reported the new phase of composition $Ni(HSeO_3)_2 \cdot 2H_2O$.

Our search for new transition metal ox-

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ides with unusual physical and chemical properties has produced another hydrated nickel selenite, $Ni_3(SeO_3)_3 \cdot H_2O$ (or $NiSeO_3 \cdot 1/3H_2O$), which has been characterized by X-ray single crystal diffraction and thermogravimetric measurements.

Experimental

Crystals of $Ni_3(SeO_3)_3 \cdot H_2O$ were grown hydrothermally in a 23-cm^3 teflon-lined stainless-steel Parr autoclave. A mixture of nickel sulfate hydrate, $NiSO_4 \cdot 6H_2O$ (2 g) and excess selenium dioxide, SeO_2 (5 g), both of analytical grade, were heated with 15 cm^3 of distilled water to 200°C for 48 hr, achieving an estimated maximum pressure of 30 bar. A very small yield (20 mg) of translucent yellow crystals was recovered from the reaction by suction filtration. The product appears to be indefinitely stable in air.

A small, irregular crystal (dimensions ca. 0.1 × 0.1 × 0.1 mm) was selected for data collection, and mounted on a glass fiber on an Enraf–Nonius automated CAD4 four circle X-ray diffractometer. Lattice constants were determined from 25 centered reflections using graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). At room temperature, the refined triclinic lattice parameters were $a = 8.118(2)$, $b = 8.423(2)$, $c = 8.531(2)$ Å, $\alpha = 123.81(2)$, $\beta = 90.59(2)$, and $\gamma = 111.43(2)°$, where the figure in parentheses represents the estimated standard deviation on the least significant figure. $V_{calc} = 438.6$ Å^3, giving a calculated density of 4.36 g/cm^3 for $Z = 2$. Intensity data were recorded in the $(\omega - 2\theta)$ scan mode with $1 \leq \theta \leq 30°$ for $-11 \leq h \leq 11$, $-11 \leq k \leq 11$, and $0 \leq l \leq 12$. The ω-scan width was $(0.80 + 0.35 \tan \theta)°$ extended by 25% on either side for background determination, and the minimum and maximum scan speeds were 1.5 and 6.7°/min, respectively. Four reflections selected for monitoring changes in crystal orientation (every 250 reflections) and intensity (every hour) showed no significant variation over the period of data collection, during which a total of 2705 reflections were measured, of which 1968 were considered observed according to the criterion $F^2 > 3\sigma(F^2)$. An empirical absorption correction (minimum value 1.16, maximum 1.91) based on ψ-scans of two reflections was applied during data reduction. All subsequent calculations assumed the centric space group $P\bar{1}$. The heavy atom positions were located from a super-sharpened Patternson function using the program SHELXS-86 (*9*) and oxygen atoms were located by repeated Fourier difference syntheses following refinement of the heavy atom positions. All the least-squares and subsidiary calculations were performed using the Oxford CRYSTALS system (*10*) on a VAX 11/750 computer. The final, full-matrix anisotropic refinement on F converged to $R = 2.85$ and $R_w = 3.27\%$ (three-term Tukey–Prince weighting scheme (*11*), with coefficients 2.4, −0.9, and 1.3). Neutral-atom complex scattering factors were input from Ref. (*12*), and a secondary extinction coefficient was included in the refinement. No possible hydrogen positions or other regions of unexplained electron density were visible in the final Fourier difference map. Final observed and calculated structure factors tables are available from the authors.

Results and Discussion

The final refined positional parameters and equivalent isotropic temperature factors for $Ni_3(SeO_3)_3 \cdot H_2O$ are presented in Table I. Anisotropic thermal factors are available as supplementary material from the authors. There are four nickel sites, all octahedrally coordinated by oxygen, and three selenium sites, all of which show typical threefold oxygen coordination. There are several distinct oxygen coordinations: O(1), O(3), O(5), O(6), O(8), and O(9) are three fold coordinated by one selenium and

TABLE I

FINAL ATOMIC PARAMETERS FOR $Ni_3(SeO_3)_3 \cdot H_2O$

Atom	x/a	y/b	z/c	U_{eqiv}
Ni(1)	0.86508(8)	0.8999(1)	0.28897(9)	0.0083
Ni(2)	−0.03787(8)	0.4537(1)	0.65334(9)	0.0078
Ni(3)	1/2	0	1/2	0.0071
Ni(4)	0	0	0	0.0067
Se(1)	0.23635(6)	0.19714(7)	0.43397(7)	0.0071
Se(2)	0.33119(6)	0.85839(7)	0.79793(7)	0.0070
Se(3)	0.33130(6)	0.47301(7)	0.17618(7)	0.0077
O(1)	0.7129(5)	0.3101(6)	0.6991(6)	0.0075
O(2)	0.2789(6)	0.3961(6)	0.9459(6)	0.0107
O(3)	0.2113(6)	0.0089(7)	0.8650(6)	0.0106
O(4)	0.4848(6)	0.9519(7)	0.7088(6)	0.0117
O(5)	0.1388(5)	0.3179(6)	0.1935(6)	0.0094
O(6)	0.8948(5)	0.0306(6)	0.7907(6)	0.0085
O(7)w	0.8747(6)	0.3979(7)	0.0834(6)	0.0142
O(8)	0.3090(5)	0.1130(6)	0.5511(6)	0.0072
O(9)	0.1732(5)	0.6214(6)	0.5974(6)	0.0097
O(10)	0.0534(5)	0.2080(6)	0.5383(6)	0.0096

Note. Triclinic: space group $P\bar{1}$ (No. 2); $a = 8.118(2)$, $b = 8.423(2)$, $c = 8.531(2)$ Å, $\alpha = 123.81(2)$, $\beta = 90.59(2)$, $\lambda = 111.43(2)°$, $V = 438.6$ Å^3, $Z = 2$. All atoms are located on general $2i$ Wyckoff site positions except Ni(3): $1f$, and Ni(4): $1a$. w: both protons are attached to the water molecule, O(7). $U_{equiv} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

two nickel atoms, while O(2) and O(4) are twofold coordinated by Se and Ni. O(10) is four-coordinated by one selenium and three nickel atoms, and O(7), which geometrical considerations and bond-strength calculations (*13*) suggest is the water molecule, is simply coordinated to a single nickel atom. The bond valence of O(7) is 0.4, neglecting proton interactions, while the bond valence sums of the other nine oxygens varies from 1.73 to 2.32. Selected bond distances and angles with e.s.d.'s are presented in Table II for the cations and in Table III for oxygens. This complex structure is a three-dimensional network, but may be described as being built up from pseudo-one-dimensional and two-dimensional units: namely, infinite edge-sharing octahedral chains in the [001] direction of the structure comprising Ni(1) and Ni(4) units which share vertices with discrete pairs of edge-sharing Ni(2) octahedra to form "sheets" in the [011] plane, and three-dimensional cross-linking of the sheets by both Ni(3) and the three SeO_3 groups. The main octahedral backbone ("1–4 chain") consists of zig-zag –[–Ni(4)–Ni(1)–Ni(1)′–]$_n$– octahedral units running along z, approximately up the c unit-cell axis. Ni(4) at (0, 0, 0) is on an inversion center, while Ni(1) has no special site symmetry. The Ni(4) octahedraon is the more regular, with nickel–oxygen distances varying from 2.00 to 2.15 Å and *cis* O–Ni–O bond angles varying from 81 to 100°. The Ni(1) octahedron is highly distorted with bond distances varying between 1.96 and 2.31 Å and angles between 71 and 108°, as opposed to the expected Ni–O contact from ionic radii sums of 2.03 Å. Discrete pairs of Ni(2) octahedra ("2–2" groups) share an edge and crosslink adjacent 1–4 chains. These units are orientated along z from (1/2, 0, 0) to 1/2, 0, 1), and may be formulated as a chain of formula –[–w–Ni(2)–Ni(2)–w–]$_n$–, where w is an H_2O unit. Nickel–oxygen bond distances

TABLE II

SELECTED BOND DISTANCE(Å)/ANGLE(°) DATA WITH e.s.d.'S FOR CATIONS IN $Ni_3(SeO_3)_3 \cdot H_2O$

Bond	Distance	Bond	Distance
Ni(1)–O(2)	1.965(4)	Ni(2)–O(7)	1.991(4)
Ni(1)–O(8)	1.991(3)	Ni(2)–O(9)	2.030(4)
Ni(1)–O(3)	2.038(4)	Ni(2)–O(9)′	2.039(4)
Ni(1)–O(6)	2.059(4)	Ni(2)–O(5)	2.111(4)
Ni(1)–O(10)	2.118(4)	Ni(2)–O(1)	2.112(4)
Ni(1)–O(10)′	2.312(4)	Ni(2)–O(10)	2.161(4)
Ni(3)–O(4)	2.031(10) × 2	Ni(4)–O(5)	2.001(7) × 2
Ni(3)–O(8)	2.032(11) × 2	Ni(4)–O(3)	2.078(9) × 2
Ni(3)–O(1)	2.097(6) × 2	Ni(4)–O(6)	2.150(11) × 2
Se(1)–O(6)	1.691(3)	Se(2)–O(4)	1.650(4)
Se(1)–O(8)	1.711(4)	Se(2)–O(9)	1.685(4)
Se(1)–O(10)	1.744(4)	Se(2)–O(3)	1.728(4)
Se(3)–O(2)	1.681(4)		
Se(3)–O(5)	1.703(3)		
Se(3)–O(1)	1.709(4)		

Angles about Ni(1)

Atom 1					
O(8)	95.7(2)				
O(3)	87.0(2)	108.7(2)			
O(6)	98.7(2)	161.6(2)	83.7(2)		
O(10)	171.6(2)	89.6(2)	97.6(2)	74.9(2)	
O(10)′	92.3(2)	70.7(2)	179.0(2)	97.1(2)	83.2(2)
Atom 2:	O(2)	O(8)	O(3)	O(6)	O(10)

Angles about Ni(2)

Atom 1					
O(9)	165.3(2)				
O(9)′	89.6(2)	79.5(2)			
O(5)	84.7(2)	87.1(2)	98.5(2)		
O(1)	97.1(2)	91.9(2)	167.5(2)	71.8(2)	
O(10)	88.4(2)	101.4(2)	90.4(2)	168.7(2)	100.3(2)
Atom 2:	O(7)	O(9)	O(9)′	O(5)	O(1)

Angles about Ni(3)

Atom 1					
O(4)′	180				
O(8)	84.2(5)	95.8(4)			
O(8)′	95.8(4)	84.2(5)	180		
O(1)	88.6(4)	91.5(4)	91.2(4)	88.8(4)	
O(1)′	91.5(4)	88.6(4)	88.8(4)	91.2(4)	180
Atom 2:	O(4)	O(4)′	O(8)	O(8)′	O(1)

Angles about Ni(4)

Atom 1					
O(5)′	180				
O(3)	92.1(4)	87.9(4)			
O(3)′	87.9(4)	92.1(4)	180		
O(6)	89.6(3)	90.4(5)	80.6(4)	99.5(5)	
O(6)′	90.4(5)	89.6(3)	99.5(5)	80.6(4)	180
Atom 2:	O(5)	O(5)′	O(3)	O(3)′	O(6)

Angles about Se(1)

Atom 1		
O(8)	104.3(2)	
O(10)	95.4(2)	92.8(2)
Atom 2:	O(6)	O(8)

Angles about Se(2)

Atom 1		
O(9)	104.1(2)	
O(3)	103.7(2)	100.8(2)
Atom 2:	O(4)	O(9)

Angles about Se(3)

Atom 1		
O(5)	105.4(2)	
O(1)	100.9(2)	93.1(2)
Atom 2:	O(2)	O(5)

TABLE III

Selected Oxygen Bond Distances(Å) and Angles(°) in $Ni_3(SeO_3)_3 \cdot H_2O$

Bond	Distance	Bond	Distance
O(1)–Se(3)	1.709(3)	O(2)–Se(3)	1.681(4)
O(1)–Ni(3)	2.097(4)	O(2)–Ni(1)	1.965(4)
O(1)–Ni(2)	2.112(6)		
O(3)–Se(2)	1.728(4)	O(4)–Se(2)	1.649(4)
O(3)–Ni(1)	2.038(4)	O(4)–Ni(3)	2.031(11)
O(3)–Ni(4)	2.077(9)		
O(5)–Se(3)	1.702(4)	O(6)–Se(1)	1.691(4)
O(5)–Ni(4)	2.001(7)	O(6)–Ni(1)	2.059(4)
O(5)–Ni(2)	2.111(4)	O(6)–Ni(4)	2.150(11)
O(7)–Ni(2)	1.991(4)	O(8)–Se(1)	1.711(3)
		O(8)–Ni(1)	1.991(3)
		O(8)–Ni(3)	2.032(10)
O(9)–Se(2)	1.685(4)	O(10)–Se(1)	1.744(4)
O(9)–Ni(2)	2.023(4)	O(10)–Ni(1)	2.118(4)
O(9)–Ni(2)′	2.039(4)	O(10)–Ni(2)	2.161(4)
		O(10)–Ni(1)′	2.311(4)

[Bond Angels]

Atoms	Angle	Atoms	Angle
Se(3)–O(1)–Ni(2)	97.4(2)	Se(3)–O(2)–Ni(1)	125.2(3)
Se(3)–O(1)–Ni(3)	121.3(4)		
Ni(2)–O(1)–Ni(3)	127.5(3)		
Se(2)–O(3)–Ni(1)	125.8(2)	Se(2)–O(4)–Ni(3)	140.5(3)
Se(2)–O(3)–Ni(4)	128.5(4)		
Ni(1)–O(3)–Ni(4)	98.2(4)		
Se(3)–O(5)–Ni(4)	124.8(4)	Se(1)–O(6)–Ni(1)	96.2(2)
Se(3)–O(5)–Ni(2)	97.7(2)	Se(1)–O(6)–Ni(4)	117.4(3)
Ni(4)–O(5)–Ni(2)	129.4(3)	Ni(1)–O(6)–Ni(4)	95.3(3)
Se(1)–O(8)–Ni(1)	104.8(2)	Se(2)–O(9)–Ni(2)	130.2(3)
Se(1)–O(8)–Ni(3)	127.2(4)	Se(2)–O(9)–Ni(2)′	115.0(2)
Ni(1)–O(8)–Ni(3)	127.2(4)	Ni(2)–O(9)–Ni(2)′	100.5(2)
Se(1)–O(10)–Ni(2)	126.8(2)	Ni(2)–O(10)–Ni(1)	116.0(2)
Se(1)–O(10)–Ni(1)	91.8(2)	Ni(2)–O(10)–Ni(1)′	125.0(2)
Se(1)–O(10)–Ni(1)′	92.4(2)	Ni(1)–O(10)–Ni(1)′	96.8(2)

vary from 1.99 to 2.16 Å and angles vary from 80 to 100°. The coordination of the Ni(1), Ni(2), and Ni(4) units is illustrated in Fig. 1 as a polyhedral representation. The Ni(3) octahedron, which is on an inversion center at (1/2, 0, 1/2) does not participate in any edge sharing with other NiO_6 units; bond lengths vary fron 2.02 to 2.10 Å; angles from 84 to 96°. Figure 2 shows the complete network of edge- and vertex-sharing nickel octahedra. The 1–4 chains and 2–2 groups are linked by corner sharing via O(5) (linking Ni(4) and Ni(2) octahedra) and via O(10) (linking two adjacent Ni(1) octahedra and one Ni(2) octahedron), hence forming effective sheets in the [011] plane. The Ni(3) octahedron shares vertices with two Ni(1) octahedra in adjacent chains (via O(8) in both cases) and one Ni(2) octahedron (via O(1)), effectively linking the [011] sheets in the

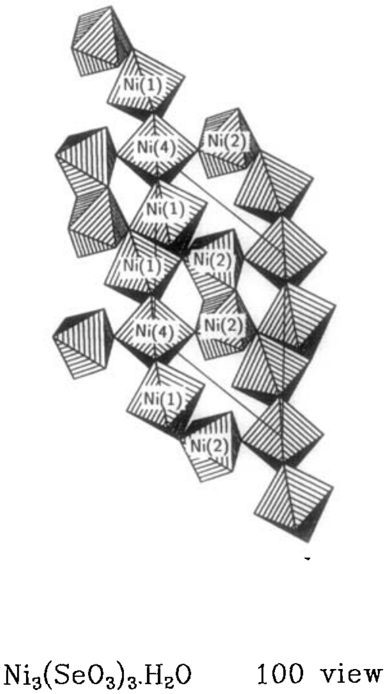

FIG. 1. STRUPLO (*17*) view of the Ni(1), Ni(2), and Ni(4) octahedra in nickel selenite hydrate, $Ni_3(SeO_3)_3 \cdot H_2O$, viewed down the [100] direction. The infinite, distorted edge-sharing 1–4 chain points along the [001] direction with Ni(4) at the unit cell corners sandwiching two Ni(1) octahedra. Discrete edge-sharing pairs of $Ni(2)O_6$ octahedra link adjacent 1–4 chains by vertex-sharing as described in the test.

[100] direction, to create a three-dimensional network. Bond valence calculations (*13*) are in good accord with Ni^{2+}, as expected, with bond valence sums for Ni(1), Ni(2), Ni(3), and Ni(4) of 1.98, 1.95, 2.04, and 1.94, respectively. The complete structure is illustrated with ORTEP in Fig. 3.

All three seleniums show the typical pseudotetrahedral SeO_3E coordination, where E is the (unobserved) hybridized lone-pair, and participate in Ni–O–Se–O–Ni linkages which involve all the oxygens except O(7), of the water molecule. The oxygen bond distances and angles around the seleniums are similar to those found in previous structural investigations of selenites (*14–17*). The average Se–O contact is 1.700 Å and the average O–Se–O angle is 100.1°. This compares well with the average values of 1.709(10) Å and 100.2(1.3)° for Se–O distances and O–Se–O angles, respectively (where the numbers in parentheses are root-mean-square deviations) found by Hawthorne *et al.* (*17*) in their survey of selenite ion geometries. For the selenium bonds in $Ni_3(SeO_3)_3 \cdot H_2O$, Se(1)–O(10) (1.744)(4) Å) is slightly longer than average, and Se(2)–O(4) (1.650(4) Å) is slightly shorter, doubtless reflecting the response of the relatively flexible selenite ion to the strained nature of the structue. The Se(1)–O(10) distance is characteristic of a Se–OH contact according to Hawthorne *et al.* (*17*); here the "overbonded" O(10), which sees three

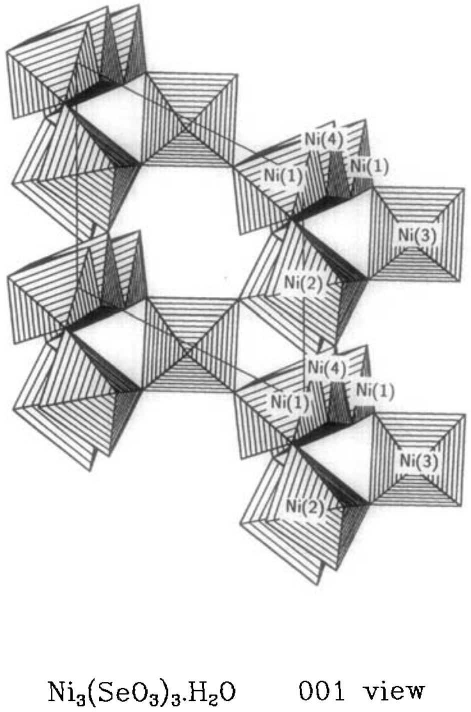

FIG. 2. STRUPLO diagram viewed down [001] showing the connectivity of the $Ni(3)O_6$ octahedra with the 1–4 chains (up the *z* axis of the unit cell) and 2–2 units in $Ni_3(SeO_3)_3 \cdot H_2O$. The vertex-sharing scheme is described in the text.

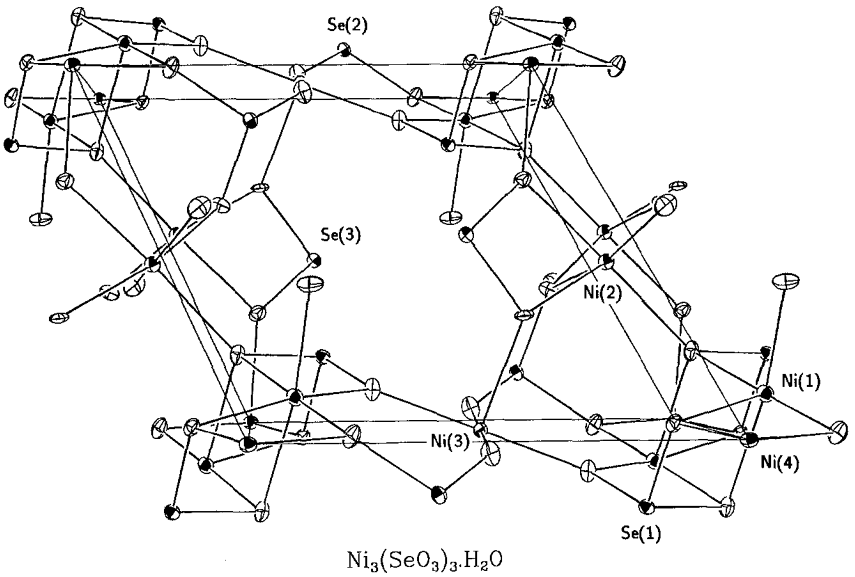

FIG. 3. ORTEP diagram of $Ni_3(SeO_3)_3 \cdot H_2O$, viewed down [100], showing heavy atom labeling scheme.

nickels as well as Se(1), is the reason for the extended selenium to oxygen contact. This flexibility in selenium geometry is reflected in bond valence sums (BVS) for the selenium cations, defined as BVS = $\Sigma\,(R/R_0)^{-N}$, with R the observed bond distance, and R_0 and N as constants. The parameters of Brown and Wu (*13*) (R_0 = 1.796, N = 4.0) give BVS values of 3.61, 3.86, and 3.76 for Se(1), Se(2), and Se(3), respectively, while the more recent values of Hawthorne *et al.* (*17*) (R_0 = 1.808, N = 5.2) give values of 3.95, 4.31, and 4.17, respectively, for the same three seleniums, compared to the expected value of 4.0.

The thermogravimetric data, collected in air with a heating rate of 10°/min, using a DuPont 990 system, show that $Ni_3(SeO_3)_3 \cdot H_2O$ loses water and selenium dioxide, without any discernable intermediates, over the broad temperature range 450–625°C (calculated weight loss = 68%, observed = 68%) to result in a final decay product of NiO.

In summary, we have found mild-condition hydrothermal reactions an effective route to new selenite-containing phases which may be characterized by single-crystal methods. Further studies are now in progress and will be reported later.

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