



# Syntheses, crystal structures, and properties of three new metal selenites Na<sub>2</sub>Co<sub>2</sub>(SeO<sub>3</sub>)<sub>3</sub>, Na<sub>2</sub>Co<sub>1.67</sub>Ni<sub>0.33</sub>(SeO<sub>3</sub>)<sub>3</sub>, and Na<sub>2</sub>Ni<sub>2</sub>(SeO<sub>3</sub>)<sub>3</sub>

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## ABSTRACT

Three new sodium cobalt (nickel) selenite compounds, namely, Na<sub>2</sub>Co<sub>2</sub>(SeO<sub>3</sub>)<sub>3</sub>, Na<sub>2</sub>Co<sub>1.67</sub>Ni<sub>0.33</sub>(SeO<sub>3</sub>)<sub>3</sub>, and Na<sub>2</sub>Ni<sub>2</sub>(SeO<sub>3</sub>)<sub>3</sub> have been hydro-/solvothermally synthesized in the mixed solvents of acetonitrile and water. Single-crystal X-ray diffraction analyses reveal that these isostructural compounds belong to the orthorhombic *Cmcm* space group and their structures feature three-dimensional open frameworks constructed by the two-dimensional layers of [MSeO<sub>3</sub>] pillared by the [SeO<sub>3</sub>]<sup>2-</sup> groups. The two different types of Na<sup>+</sup> ions reside in the intersecting two-dimensional channels parallel to the *a*- and *c*-axes, respectively. Their thermal properties have been investigated via TGA–DSC. The magnetic measurements indicate the existence of the antiferromagnetic interactions in these compounds.

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## 1. Introduction

Metal selenites have received considerable attention in the past two decades, in which selenium is found in a formal oxidation state of IV. Depending on the different conditions in solutions [1,2], selenium(IV) may exist in various forms such as H<sub>2</sub>SeO<sub>3</sub>, HSeO<sub>3</sub><sup>-</sup>, SeO<sub>3</sub><sup>2-</sup>, and Se<sub>2</sub>O<sub>5</sub><sup>2-</sup> [3–6]. Of particularly interesting is SeO<sub>3</sub><sup>2-</sup>, in which the Se<sup>4+</sup> ion with stereochemically active lone pair of electrons adopts the asymmetric coordination geometry of  $\psi$ -SeO<sub>3</sub>, which may lead to noncentrosymmetric structures with consequent interesting physical properties, such as nonlinear optical second harmonic generation (SHG) [7–10]. The transition metal selenites are of special interest due to their unique magnetic properties. The transition metal selenites incorporating alkali (or alkaline earth) metal ions have been reported mostly by Giester and Wildner, formulated as A<sub>x</sub>B<sub>y</sub>(SeO<sub>3</sub>)<sub>2</sub> (A=alkali metals or alkaline earth metals, B=transition metals) [5,11–17], A<sub>x</sub>B<sub>y</sub>(SeO<sub>3</sub>)<sub>3</sub> [18–23], A<sub>x</sub>B<sub>y</sub>(SeO<sub>3</sub>)<sub>4</sub> [17,23,24], A<sub>x</sub>B<sub>y</sub>(SeO<sub>3</sub>)<sub>6</sub> [25–28], and A<sub>x</sub>B<sub>y</sub>(SeO<sub>3</sub>)<sub>8</sub> [25], respectively. A variety of lanthanide selenites and actinide selenites have also been studied [29–32]. In addition, organic–inorganic hybrid materials by incorporating organic carboxylate ligands into metal selenite moieties have been described [33,34]. In our attempt to synthesize the organic–inorganic hybrid transition metal selenites, we unexpectedly

obtained three new inorganic transition metal selenite compounds containing the sodium ions, namely, Na<sub>2</sub>Co<sub>2-x</sub>Ni<sub>x</sub>(SeO<sub>3</sub>)<sub>3</sub> (*x*=0 (**1**), 0.33 (**2**), 2 (**3**)). Herein we report their syntheses, crystal structures, and thermal and magnetic properties.

## 2. Experimental section

### 2.1. Materials and methods

CoCl<sub>2</sub>·6 H<sub>2</sub>O (99%), NiCl<sub>2</sub>·6H<sub>2</sub>O (98%), Na<sub>2</sub>SeO<sub>3</sub> (98%), 2,3-pyrazinedicarboxylic acid (98%), pyridine-3,5-dicarboxylic acid (98%), 1,10-phenanthroline (99%), and acetonitrile (99%) were used. All of the chemical reagents were obtained from commercial sources and used without further purification. Co, Ni, Na, Se analyses were carried out with an ICPQ-100 spectrometer. Energy dispersive X-ray spectroscopy (EDX) was measured by JEOL-6700F scanning electron microscope. IR spectra were recorded with a Magna 750FT-IR spectrometer using KBr pellets in the range 4000–400 cm<sup>-1</sup>. Simultaneous thermogravimetric analysis and differential scanning calorimetry (TGA–DSC) were carried out with a NETZSCH STA 449F3 unit at a heating rate of 10 °C/min under a nitrogen atmosphere. The powder X-ray diffraction patterns were collected in the angular range of 2θ=10–80° with a step size of 0.02° on the Rigaku MiniFlexII X-ray diffractometer. The variable-temperature magnetic susceptibilities (2–300 K) were measured with a model MPMS6000 superconducting extraction sample magnetometer under a field

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of 1000 Oe with the crystalline samples kept in a capsule for weighing.

## 2.2. Syntheses of compounds **1**, **2**, and **3**

Compounds **1**, **2**, and **3** were synthesized by employing the hydro-/solvothoermal methods in similar reaction conditions and isolation procedures. A mixture of reactants in a mixed solvent of 3 mL acetonitrile and 3 mL distilled water was stirred to assure homogeneity and sealed in an autoclave equipped with a Teflon liner (28 mL). After 7 days of reaction at 140 °C, the crystals were isolated by filtration and washed with distilled water. The powder X-ray diffraction study for the compounds indicated that all of the three compounds are single-phased.

### 2.2.1. Preparation of $\text{Na}_2\text{Co}_2(\text{SeO}_3)_3$ (**1**)

The reagents are  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.118 g, 0.5 mmol),  $\text{Na}_2\text{SeO}_3$  (0.173 g, 1 mmol), and 2,3-pyrazinedicarboxylic acid (0.088 g, 0.52 mmol). The dark purple crystals of **1** were isolated in 49.62% yield (0.067 g) calculated based on Co. IR (KBr,  $\text{cm}^{-1}$ ): 2920 (vw), 2849 (vw), 1636 (v), 1617 (s), 1384 (s), 1356 (w), 1021 (w), 715 (br), 619 (m), 527 (w), 476 (w).

### 2.2.2. Preparation of $\text{Na}_2\text{Co}_{1.67}\text{Ni}_{0.33}(\text{SeO}_3)_3$ (**2**)

The reagents are  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.071 g, 0.3 mmol),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.049 g, 0.2 mmol),  $\text{Na}_2\text{SeO}_3$  (0.177 g, 1.02 mmol), and 2,3-pyrazinedicarboxylic acid (0.089 g, 0.52 mmol). The green crystals of **2** were obtained in 40.14% yield (0.055 g) (based on Co). IR (KBr,  $\text{cm}^{-1}$ ): 2924 (vw), 2827 (vw), 2346 (m), 1606 (s), 1384 (s), 1109 (w), 1016 (w), 763 (w), 712 (w), 660 (w), 472 (w). The ratio of Co and Ni were established as 1.67:0.33 by EDX measurements.

### 2.2.3. Preparation of $\text{Na}_2\text{Ni}_2(\text{SeO}_3)_3$ (**3**)

The reagents are  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.119 g, 0.5 mmol),  $\text{Na}_2\text{SeO}_3$  (0.173 g, 1 mmol), pyridine-3,5-dicarboxylic acid (0.084 g, 0.5 mmol), and 1,10-phenanthroline (0.106 g, 0.59 mmol). The green crystals of **3** were obtained in 35.29% yield (0.048 g) (based on Ni). IR (KBr,  $\text{cm}^{-1}$ ): 2920 (vw), 2029 (w), 1772 (vw), 1637 (s),

1617 (s), 1384 (m), 1018 (w), 818 (w), 722 (m), 726 (m), 622 (s), 475 (m).

The pure powders of **1** and **3** could also be synthesized by the same reactions in the absence of organic reagents.

## 2.3. Determination of crystal structures

The single crystal X-ray diffraction studies were performed on a Rigaku SCX-mini CCD diffractometer for compounds **1** and **2**, and on a Rigaku Saturn724 CCD diffractometer for compound **3** equipped with graphite monochromated  $\text{MoK}\alpha$  radiation ( $\lambda=0.71073$  Å). Intensity data were collected by the narrow frame method at room temperature and corrected for Lorentz and polarization effects as well as for absorption by the SADABS program. All the structures were solved by direct methods and refined by full-matrix least-squares cycles in SHELX-97 [35]. The crystallographic data and structural refinement parameters for the three compounds are summarized in Table 1. The atomic coordinates are listed in Table 2 for compounds **1**, **2**, and **3**.

## 3. Results and discussion

### 3.1. Synthesis

The title compounds were synthesized hydro-/solvothermally in the mixed solvents of acetonitrile and distilled water in a volume proportion of 1:1. It is noteworthy that the presence of organic carboxylic acids in the reactions is important not only for the phase purity but also for the crystallinity, although they did not enter the structures of final products. For instance, we could obtain the crystals of compounds **1** and **3** in the presence of organic acids, while the pure phases of compounds **1** and **3** in powder form were formed in the same synthetic conditions but without adding any kind of organic acids. Note that the pH values for the reactant mixtures were  $\sim 6$  with organic acids and  $\sim 9$  without adding organic acids, respectively. It is likely the pH values also influence the formation of the crystals of compounds **1** and **3**. More interestingly, the crystals of **1** and **3** were grown in the presence of 2,3-pyrazinedicarboxylic acid and pyridine-3,5-

**Table 1**  
Summary of the crystal data and structure refinements for compounds **1**, **2**, and **3**.

	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	$\text{Na}_2\text{Co}_2\text{O}_9\text{Se}_3$	$\text{Na}_2\text{Co}_{1.67}\text{Ni}_{0.33}\text{O}_9\text{Se}_3$	$\text{Na}_2\text{Ni}_2\text{O}_9\text{Se}_3$
Formula weight	544.72	544.65	544.28
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	<i>Cmcm</i>	<i>Cmcm</i>	<i>Cmcm</i>
<i>T</i> /K	293	293	293
$\lambda$ /Å	0.71073	0.71073	0.71073
<i>a</i> /Å	7.551(5)	7.5156(16)	7.464(4)
<i>b</i> /Å	11.147(8)	11.107(3)	11.055(5)
<i>c</i> /Å	10.270(8)	10.2320(14)	10.180(5)
<i>V</i> /Å <sup>3</sup>	864.4(11)	854.1(3)	840.0(7)
<i>Z</i>	4	4	4
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	4.186	4.236	4.304
$\mu$ /mm <sup>-1</sup>	16.602	16.888	17.616
<i>F</i> (0 0 0)	1000	1001	1008
Measured refls.	3302	3230	3596
Independent refls.	561	556	550
No. of parameters	59	59	59
<i>GOF</i>	1.079	1.071	1.079
<i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> ): <i>R</i> 1, <i>wR</i> 2]	0.0300, 0.0999	0.0316, 0.0956	0.0320, 0.0758
<i>R</i> indices (all data): <i>R</i> 1, <i>wR</i> 2	0.0312, 0.1008	0.0337, 0.0972	0.0353, 0.0777
ICSD no.	4,21,690	4,21,692	4,21,691

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad wR2 = \{ \sum w[(F_o)^2 - (F_c)^2]^2 / \sum w(F_o)^2 \}^{1/2}.$$

dicarboxylic acid, respectively, while using 2,3-pyrazinedicarboxylic acid instead of pyridine-3,5-dicarboxylic acid in the synthesis of compound **3** resulted in an unidentified powder only. Therefore, the different dicarboxylic acids have some influence in the formation of final products. Also note that the compounds  $K_2Co_2(SeO_3)_3$  [20],  $K_2[Co_2(SeO_3)_3] \cdot 2H_2O$ , and  $K_2[Ni_2(SeO_3)_3] \cdot 2H_2O$  [18] have the same formula of anionic parts but totally different structures compared to the title compounds, however, in their preparation no organic acid was added, and the reactions were carried out at higher temperature. Unluckily, we tried to use the  $K^+$  reagent instead of  $Na^+$  to synthesize the isostructural potassium-transition metal selenites in similar reaction conditions but failed.

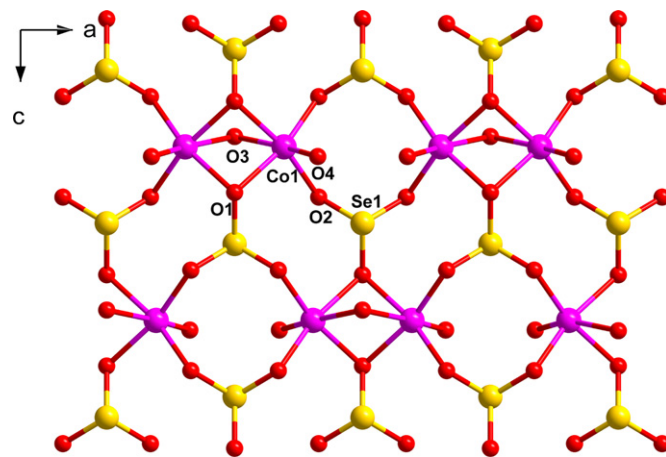
**Table 2**  
Atomic coordinates ( $\times 10^4$ ) for compounds **1**, **2**, and **3**.

Atoms	x	y	z
<b>1</b>			
Se(1)	0	2346(1)	5299(1)
Se(2)	0	5155(1)	1999(2)
Co(1)	1934(2)	2430(1)	2500
O(1)	0	1638(5)	3813(6)
O(2)	1714(6)	1663(4)	6050(4)
O(3)	0	3811(9)	2770(11)
O(4)	-1736(11)	5812(7)	2762(11)
Na(1)	0	-211(5)	2500
Na(2)	2697(12)	0	5000
<b>2</b>			
Se(1)	0	2353(1)	5301(1)
Se(2)	0	5155(1)	1992(2)
M	1922(1)	2428(1)	2500
O(1)	0	1643(5)	3811(5)
O(2)	1727(6)	1668(4)	6052(4)
O(3)	0	3792(8)	2779(8)
O(4)	-1750(10)	5815(7)	2753(10)
Na(1)	0	-208(5)	2500
Na(2)	2708(11)	0	5000
<b>3</b>			
Se(1)	0	2367(1)	5305(1)
Se(2)	0	5152(1)	1976(1)
Ni(1)	1898(1)	2426(1)	2500
O(1)	0	1637(4)	3814(4)
O(2)	1732(4)	1674(3)	6067(3)
O(3)	0	3806(7)	2773(9)
O(4)	-1766(7)	5811(5)	2758(8)
Na(1)	0	-214(3)	2500
Na(2)	2702(8)	0	5000

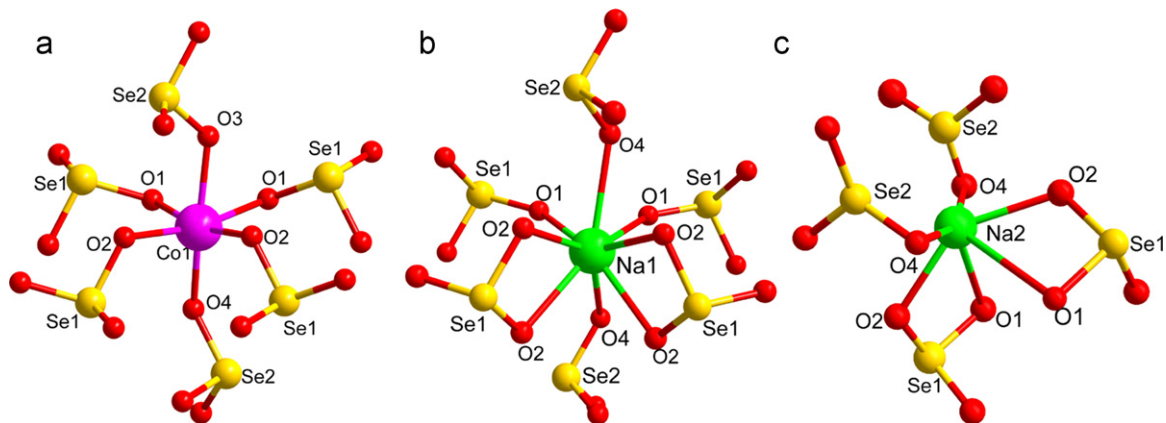
$M=0.835 Co+0.165 Ni$ .

### 3.2. Crystal structures

Single crystal X-ray analyses reveal that compounds **1**, **2**, and **3** crystallize in the space group  $Cmcm$  and they are isostructural. Therefore, only the structure of compound **1** as a representative is described in detail. The asymmetric unit of compound **1** contains half a  $Co^{2+}$  ion, half a  $Se(1)O_3^{2-}$  group, a quarter of  $Se(2)O_3^{2-}$  group, a quarter of  $Na(1)^+$  ion, and a quarter of  $Na(2)^+$  ion, respectively. The  $Co^{2+}$  ion is coordinated by six oxygen atoms from four  $Se(1)O_3^{2-}$  groups and two  $Se(2)O_3^{2-}$  groups in an unidentate fashion, respectively (Fig. 1a). The  $Co-O$  bond lengths range from 2.069(4) to 2.175(5) Å and the  $O-Co-O$  angles are in the range  $75.7(3)-167.35(17)^\circ$ . Two  $CoO_6$  octahedra share two O(1) and one O(3) to form a  $Co_2O_9$  dimer. The  $Se(1)O_3^{2-}$  and  $Se(2)O_3^{2-}$  groups are tetradentate and bridge four  $Co^{2+}$  ions, respectively. The O(1) atom from  $Se(1)O_3^{2-}$  group and O(3) atom from  $Se(2)O_3^{2-}$  group are bidentate metal linkers whereas the two O(2) atoms from  $Se(1)O_3^{2-}$  group and the two O(4) atoms from  $Se(2)O_3^{2-}$  group are unidentate, respectively. The disordered  $Se(2)O_3^{2-}$  group is randomly distributed on one of the two positions [20]. The  $SeO_3^{2-}$  trigonal pyramids exhibit bond lengths with a mean value of 1.696 Å, which is in good agreement with the values observed for related selenite compounds [18,20]. The interconnections of  $Co^{2+}$  ions by bridging  $Se(1)O_3^{2-}$  groups result in a two-dimensional layer (2D) of  $[CoSe(1)O_3]$  along the  $ac$  plane, Fig. 2. Four-membered  $Co_2O_2$  rings and eight-membered  $Co-(O-Se(1)-O)_2-Co$  rings are evident in the 2D layer. The  $Co...Co$  separation within a  $Co_2O_2$  four-membered ring is



**Fig. 2.** The two-dimensional layer of  $[CoSe(1)O_3]$  in structure **1** along the  $ac$  plane.



**Fig. 1.** The coordination environments of Co ion (a), Na(1) ion (b), and Na(2) ion (c) in structure **1**.



2.928 Å. The  $\text{CoSe(1)O}_3$  layers are further cross-linked by  $\text{Se(2)O}_3$  groups into a pillared layered architecture, Fig. 3a. It is interesting that compound **1** reveals intersecting two-dimensional channels parallel to the  $a$ - and  $c$ -axis, respectively. A rough square cross section of  $4.1 \times 5.7$  Å constructed by 16-membered  $\text{Co}_4\text{Se(1)}_2\text{Se(2)}_2\text{O}_8$  ring is evident for the channels parallel to the  $a$ -axis

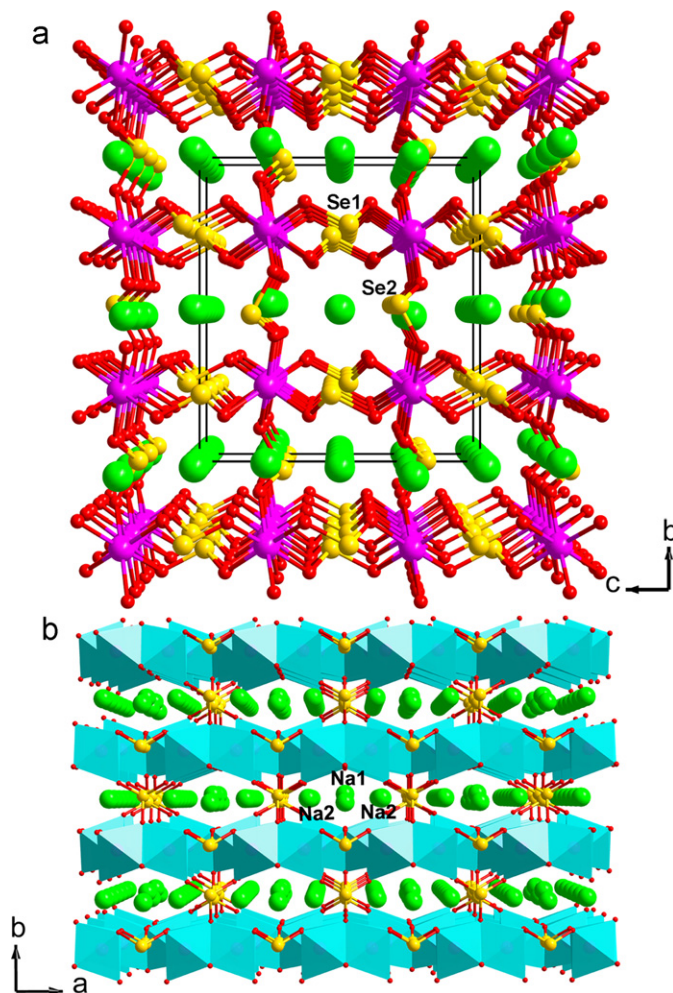


Fig. 3. (a) View of the three-dimensional (3D) framework of compound **1** along the  $a$ -axis and (b) polyhedral view of the 3D framework of compound **1** along the  $c$ -axis.

(Fig. 4a), whereas the 14-membered  $\text{Co}_4\text{Se(1)Se(2)}_2\text{O}_7$  rings comprising a rough elliptical cross section of  $5.7 \times 7.5$  Å are present parallel to the  $c$ -axis (Fig. 4b). The lone pair electrons of the  $\text{Se}^{4+}$  ions are oriented toward the interior of channels. The  $\text{Na(1)}^+$  ions and  $\text{Na(2)}^+$  ions are located in the channels.  $\text{Na(1)}^+$  ion is surrounded by eight oxygen atoms to form a  $\text{Na(1)O}_8$  polyhedron; six of them are from four different  $\text{Se(1)O}_3$  groups, while the other two oxygen atoms are from two different  $\text{Se(2)O}_3$  groups (Fig. 1b). The  $\text{Na(2)}^+$  ion is surrounded by six oxygen atoms to form a  $\text{Na(2)O}_6$  polyhedron; four of them are from two different  $\text{Se(1)O}_3$  groups, while the other two oxygen atoms are from two different  $\text{Se(2)O}_3$  groups (Fig. 1c). The Na–O distances range from 2.269(5) to 2.995(8) Å. In each channel parallel to the  $c$ -axis, the  $\text{Na(1)}^+$  ions are in the middle and the  $\text{Na(2)}^+$  ions are in the two sides of the channel, Fig. 3b. In fact, the reported compounds, namely  $\text{K}_2\text{Co}_2(\text{SeO}_3)_3$  [20],  $\text{K}_2[\text{Co}_2(\text{SeO}_3)_3] \cdot 2\text{H}_2\text{O}$ , and  $\text{K}_2[\text{Ni}_2(\text{SeO}_3)_3] \cdot 2\text{H}_2\text{O}$  [18] contain the same anionic moiety of  $\text{M}_2(\text{SeO}_3)_3^{2-}$  ( $\text{M}=\text{Co}, \text{Ni}$ ) as the title compounds, however, their structures are different. The compound  $\text{K}_2\text{Co}_2(\text{SeO}_3)_3$  crystallizing in the space group  $P6_3/mmc$  features a two-dimensional double-layer structure of  $\text{Co}_2(\text{SeO}_3)_3^{2-}$ . The  $\text{Co}^{2+}$  ions are connected by  $\text{Se(1)O}_3$  to form a single layer of cobalt selenite with the 12-membered  $\text{Co}_3\text{Se(1)}_3\text{O}_6$  rings along the  $ab$  plane. Two single layers of the cobalt selenite are further linked by  $\text{Se(2)O}_3$  groups to give rise to a two-dimensional double-layer of  $\text{Co}_2(\text{SeO}_3)_3^{2-}$  (Fig. S6). Whereas the structures of  $\text{K}_2[\text{M}_2(\text{SeO}_3)_3] \cdot 2\text{H}_2\text{O}$  ( $\text{M}=\text{Co}, \text{Ni}$ ) feature three-dimensional open frameworks with one-dimensional honeycomb-like channels along the  $c$ -axis constructed by 24 membered  $\text{Co}_6\text{Se}_6\text{O}_{12}$  rings, which are quite different from that of the title compounds (Fig. S7).

#### 4. Characterizations and properties

##### 4.1. IR spectra

The IR spectra of the title compounds were studied in the range  $4000\text{--}400\text{ cm}^{-1}$ . Three different groups of bands attributed to the vibrational modes of the selenite anions were observed [36]. The symmetric  $\nu_s(\text{Se-O})$  stretching bands are detected at  $1016\text{--}1021\text{ cm}^{-1}$ , however, the asymmetric  $\nu_{as}(\text{Se-O})$  stretching bands are split, due to the inherently asymmetric  $\text{SeO}_3^{2-}$  anion and appears as a group of bands around  $818\text{--}712\text{ cm}^{-1}$ . Finally, those from  $470\text{--}660\text{ cm}^{-1}$  originated from the deformation vibrations of  $\delta(\text{O-Se-O})$ . The obtained results are similar with those of the other related metal selenite compounds [37,38].

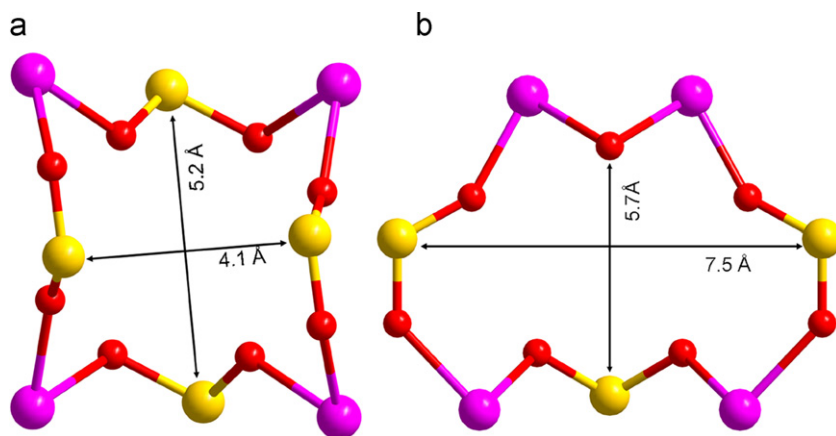


Fig. 4. (a) A rough square cross section of  $4.1 \times 5.7$  Å parallel to the  $a$ -axis constructed by 16-membered  $\text{Co}_4\text{Se(1)}_2\text{Se(2)}_2\text{O}_8$  ring in compound **1**; (b) the 14-membered  $\text{Co}_4\text{Se(1)Se(2)}_2\text{O}_7$  rings comprising a rough elliptical cross section of  $5.7 \times 7.5$  Å parallel to the  $c$ -axis in compound **1**.

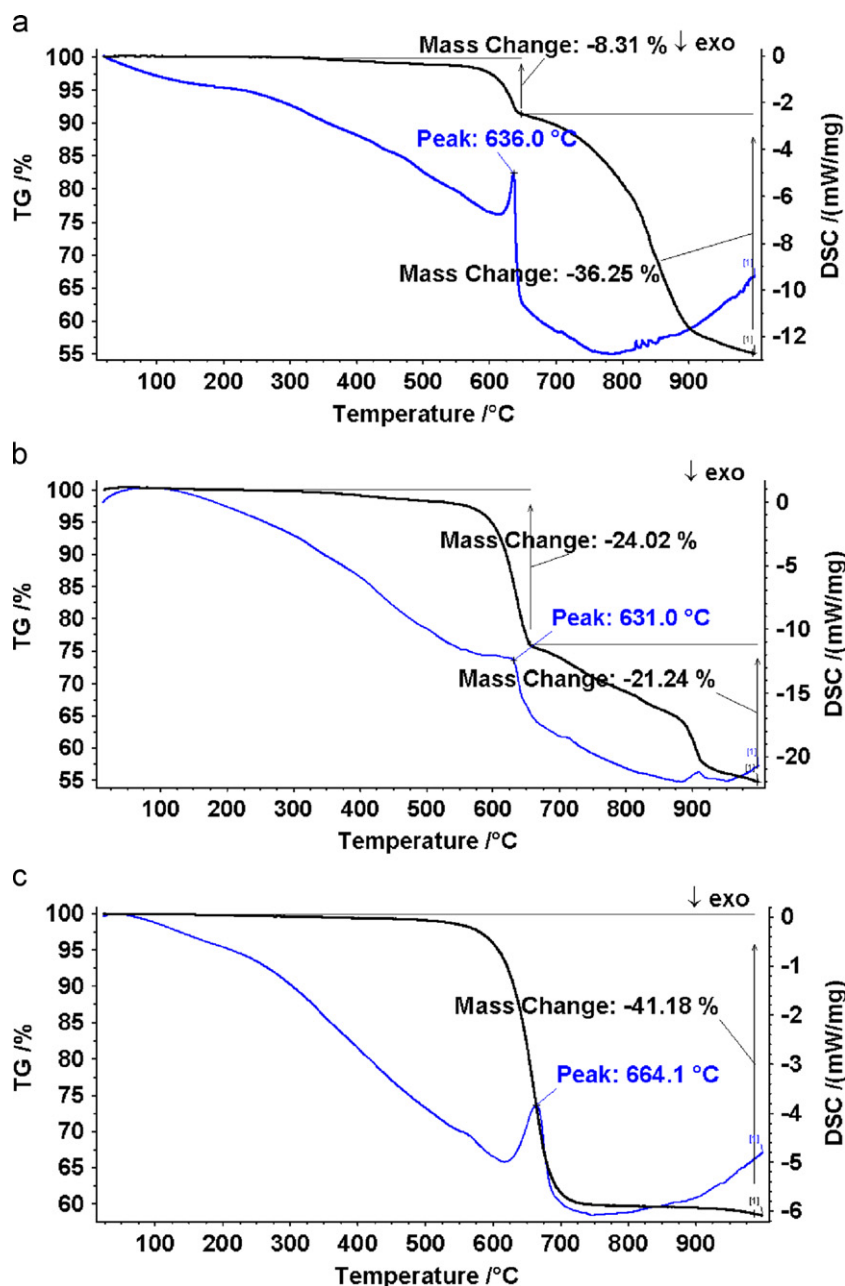


Fig. 5. The TGA and DSC curves for compounds **1** (a), **2** (b), and **3** (c).

#### 4.2. Thermal stability studies

The thermal stabilities of compounds **1–3** were examined by TGA–DSC in a  $N_2$  atmosphere from 25 to 1000 °C. As shown in Fig. 5, the TGA curves indicated that compounds **1** and **2** displayed two steps of weight losses, while compound **3** showed one main step of weight loss. Compound **1** was stable up to 320 °C, and then there was a stepwise weight loss of one  $O_2$  at first. The subsequent weight loss corresponded to the release of two  $SeO_2$  molecules. The total observed weight loss of 44.56% was in good agreement with the calculated values (46.6%). There was one sharp accompanying exothermic signal at 336 °C on the DSC curve. Compound **2** released one  $O_2$  and one  $SeO_2$  [39] for the first step from around 320 to 650 °C with the weight loss of 24.02% (the theoretical value is 26.2%). The second step weight loss corresponds to the release of another  $SeO_2$  molecule. The total observed weight loss of 45.26% was in good agreement with the

calculated values (46.6%). On the DSC curve of compound **2**, there was one weak accompanying exothermic signal at 631 °C. However, the TGA curves of compound **3** showed only one main step of weight loss which corresponds to the loss of two  $SeO_2$  molecules. The observed weight loss of 41.18% for **3** was in good agreement with the calculated values (40.7%). And there was one main exothermic signal at 664 °C for **3** on the DSC curve. The residual solids contain CoO for **1**, NiO for **3**,  $Co_{0.83}Ni_{0.17}O$  for **2**, and unidentified phases.

#### 4.3. Magnetic measurements

The results for the temperature-dependent magnetic measurements of compounds **1**, **2**, and **3** are shown in Fig. 6 in the temperature range 2–300 K at 1000 Oe applied field. For the three compounds, the thermal evolution of the molar magnetic

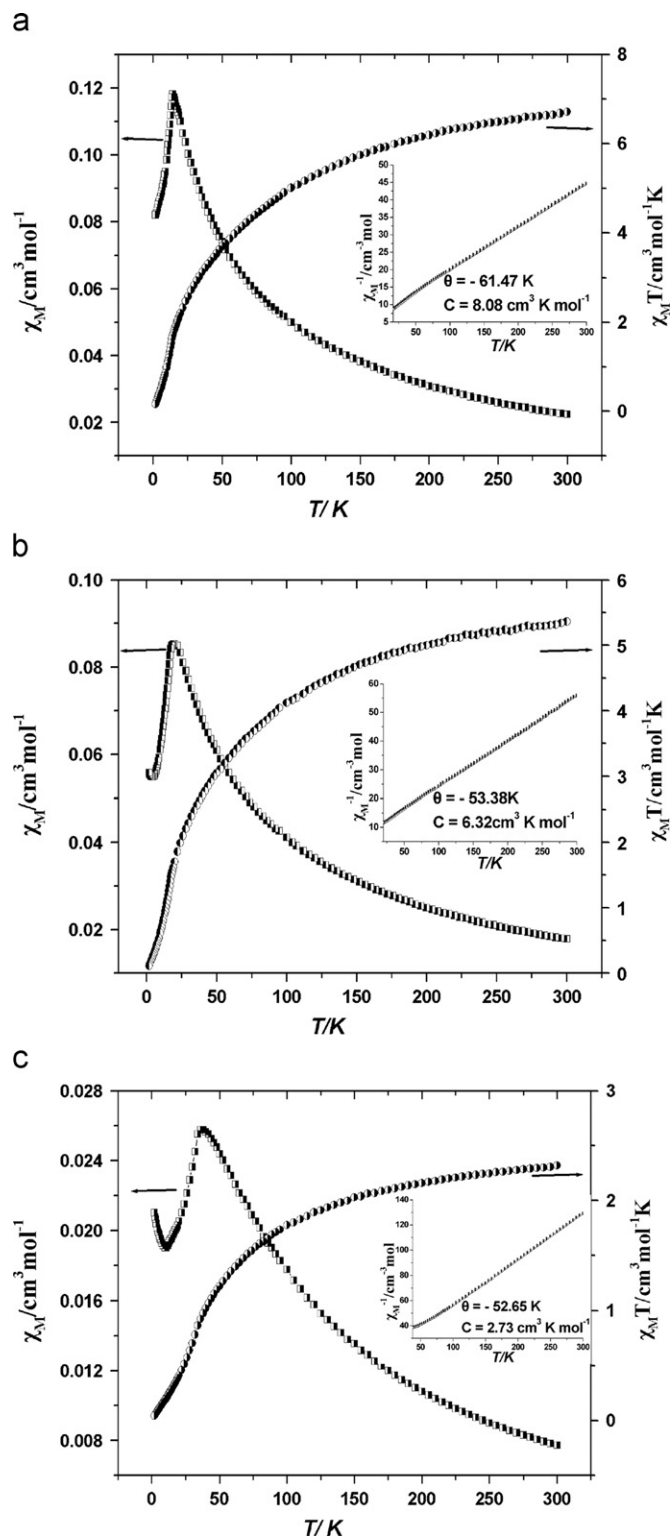


Fig. 6. Temperature dependence of  $\chi_M T$ ,  $\chi_M$  for compounds **1** (a), **2** (b), and **3** (c). The insets show the  $\chi_M^{-1}$  versus  $T$ .

susceptibility,  $\chi_M$ , shows a maximum in the 14–35 K range. For **1**, the thermal evolution of the molar magnetic susceptibility  $\chi_M$  shows the maximum at 14 K, and below that temperature, the susceptibility decreases continuously until 2 K. It reveals a room-temperature  $\chi_M T$  value of  $6.62 \text{ cm}^3 \text{ K mol}^{-1}$ , which is larger than isolated spin  $\text{Co}^{2+}$  cations ( $3.75 \text{ cm}^3 \text{ K mol}^{-1}$ ) [40]. This larger value is the result of contributions to the susceptibility from orbital angular momentum at high temperatures [39]. For **2**, it

shows the maximum at 19 K, and below that temperature the susceptibility decreases continuously until 6 K. After that there is a little jump increase at 2 K. It reveals a room-temperature  $\chi_M T$  value of  $5.40 \text{ cm}^3 \text{ K mol}^{-1}$ . For **3**, the thermal evolution of the molar magnetic susceptibility  $\chi_M$  shows the maximum at 35 K, and below that temperature the susceptibility decreases continuously until 9 K. But there is a continuously increase until 2 K. The value of  $\chi_M T$  is  $2.30 \text{ cm}^3 \text{ K mol}^{-1}$ , which is much lower than the above three. As shown in Fig. 6, upon lowering the temperature, all of the three  $\chi_M T$  decreases slowly between 300 and 100 K, and then rapidly decreases to the minimum of  $0.16 \text{ cm}^3 \text{ K mol}^{-1}$  for **1**,  $0.14 \text{ cm}^3 \text{ K mol}^{-1}$  for **2**, and  $0.04 \text{ cm}^3 \text{ K mol}^{-1}$  for **3** at 2 K, indicating an overall antiferromagnetic coupling [41,42]. For **1**, the molar magnetic susceptibility higher than 14 K follows the Curie–Weiss law ( $\chi_M = C/(T - \theta)$ ) with  $C = 8.08 \text{ cm}^3 \text{ K mol}^{-1}$ , and a negative  $\theta = -61.47 \text{ K}$ , Fig. 6a. These features confirm the existence of the antiferromagnetic interactions and the effect of the spin–orbit coupling known for octahedral Co ions [43–45]. For **2**, the molar magnetic susceptibility higher than 22 K follows the Curie–Weiss law ( $\chi_M = C/(T - \theta)$ ) with  $C = 6.32 \text{ cm}^3 \text{ K mol}^{-1}$ , and a negative  $\theta = -53.38 \text{ K}$ , Fig. 6b. For **3**, the molar magnetic susceptibility higher than 40 K follows the Curie–Weiss law ( $\chi_M = C/(T - \theta)$ ) with  $C = 2.73 \text{ cm}^3 \text{ K mol}^{-1}$ , and a negative  $\theta = -52.65 \text{ K}$ , Fig. 6c. Furthermore, the large negative  $\theta$  value suggests a dominant antiferromagnetic coupling [46] between the adjacent Ni(II) ions [47,48] for **3**.

## 5. Conclusion

Three new isostructural transition metal selenites, namely  $\text{Na}_2\text{Co}_{2-x}\text{Ni}_x(\text{SeO}_3)_3$  ( $x = 0$  (**1**),  $0.33$  (**2**),  $2$  (**3**)) have been synthesized under mild hydro-/solvothetical conditions. Their crystal structures feature three-dimensional open frameworks of  $[\text{M}_2(\text{SeO}_3)_3]^{2-}$  ( $M = \text{Co}, \text{Co/Ni}, \text{Ni}$ ) constructed by the  $[\text{SeO}_3]^{2-}$  groups bridging the two-dimensional layers of  $[\text{MSeO}_3]$ . The intersecting two-dimensional channels are occupied by  $\text{Na}^+$  ions. The thermal properties and the magnetic properties of compounds **1–3** have been investigated. The magnetic measurements indicate the existence of the antiferromagnetic interactions in compounds **1–3**.

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## Appendix A. Supporting Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2010.06.020.

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